SENIOR CHEMISTRY

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BY

G. H. BAILEY, D.Sc. Lond., Ph.D. Heidelberg
LATE LECTURER IN CHEMISTRY AT THE VICTORIA UNIVERSITY OF MANCHESTER

AND

H. W. BAUSOR, M.A. Camb., F.C.S., A.I.C.
LATE SCHOLAR OF CLARE COLLEGE, CAMBRIDGE
AUTHOR OF "PRELIMINARY CHEMISTRY," "CHEMICAL CALCULATIONS," ETC.
JOINT AUTHOR OF "ELEMENTARY QUANTITATIVE ANALYSIS," ETC.

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PREFACE.

This book has been prepared with the object of providing a clear and adequate account of the elements of systematic chemistry and of the fundamental chemical laws, together with a good supply of experimental illustrations which the student can work through in the laboratory. Without a suitable laboratory course dealing especially with the fundamentals of the subject the student learns nothing of any value; and, on the other hand, without a proper text-book account of systematic chemistry the student's knowledge is necessarily vague, indefinite, and disjointed.

The book is divided into four sections. Section I. is an Introductory Course of the approved type, based on a series of experiments by which the fundamental principles of the science are established in their proper sequence. Special care has been devoted to the treatment of the Laws of Constant and Multiple Proportions, Chemical Equivalents, Avogadro's Hypothesis, and the meaning and use of Chemical Formulae and Equations.

Sections II. and III. contain a systematic treatment of the non-metals and of most of the commoner metals, illustrated by numerous experiments; Section III. also includes chapters on Molecular and Atomic Weight Determination, the Phenomena of Electrolysis, and the Modes of Formation of Salts.

Section IV. consists of a chapter on Chemical Calculations with full discussion of the principles and methods involved.

This book has been prepared by Mr. H. W. Bausor, M.A., and is based on the well-known *Tutorial Chemistry* by Dr. G. H. Bailey. The alterations have, however, been very extensive both as regards contents and methods of treatment so that this work is essentially a new book.

NOTE TO THE SECOND EDITION.

In this edition a few notes on copper have been inserted as an Appendix. Otherwise no alteration of importance has been made.

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SECTION I.—INTRODUCTORY.

CHAPTER I.

PHYSICAL AND CHEMICAL CHANGES.

1. **The Method of Scientific Inquiry.**—Let a person unacquainted with the aims and the conduct of scientific inquiry examine some material object, say a mineral, a piece of rock, or a pebble from the sea-shore, and let him then detail the points of interest which occur to him as the result of his examination. He may be struck by its form, its colour, its hardness, the nature of its surface, or he may be disposed to ask whence it came and how.

In what respects do his questionings differ from those of one trained in the methods of scientific investigation? In this, that the scientist is accustomed to grouping his observations, he is trained by experience to the recognition of likenesses and unlikenesses in such bodies so as to reject the trivial details, and hold firmly to the essential and characteristic ones.

Investigation by a process of comparison and classification, however, opens up such a wide field, that it becomes necessary to proceed step by step, and press the inquiry along well-defined lines, each with a distinct purpose.

The geologist, desirous of determining the history of the strata, will devote himself to the observation of existing strata, their essential and prevailing characters, their origin and mode of formation. The biologist, on the other hand, studies the structure of living organisms, classifying them according to their forms and functions, and tracing historically the occurrence and evolution of the different types. The physicist interests himself with the phenomena associated with matter, whilst the chemist deals with matter itself and its identification.

Now to all these, such objects as we have mentioned in the opening paragraph will appeal in a variety of ways. A piece of chalk, limestone, or marble are very different objects to the geologist, but may be much the same thing to the chemist if he finds them to be composed of the same kind of matter. A piece of glass rubbed briskly with silk becomes capable of attracting small light bodies; this observation is of little direct importance to the chemist if he finds that the substance of the glass has not changed or its mass become greater, though to the physicist such an observation may be of great significance. A piece of iron, so far as the chemist is concerned, retains its identity as iron whether it be in the form of a solid bar, the finest wire, or an impalpable powder; it may grow warmer and expand or by cooling contract; it may be endowed with the property of attracting other particles of iron or not, and yet its composition and mass may remain unchanged. So long as any modification of aspect or behaviour is such as experience has taught him belong to matter which he identifies as *iron* he maintains that no alteration in substance has taken place.

To sum up, we may say that the method of scientific inquiry as applied to Chemistry consists in experiment, observation and inference.

2. Transmutation of Metals.—The earlier chemists believed that they could change the baser metals into noble metals, quicksilver into gold or lead into silver, and most of their researches were pursued with this object in view. The more searching methods of inquiry adopted in later times have, however, shown that their conclusions were fallacious.

So also, even to the time of Lavoisier, towards the close of the eighteenth century, chemists failed to realise what takes place when iron rusts or metals burn, although an actual change of substance has taken place, and matter is indeed added to the metals during the process.

These misunderstandings arose from two main sources:

(1) Failure to appreciate the *essential and characteristic* properties of the substance under consideration.

(2) Failure to test whether any *apparent* alteration of substance had been accompanied by increment or loss of substance during the experiment.

At each step the balance must be called upon to say whether any increment or loss of substance has taken place, and if so the source of this change in mass must be traced.

All conclusions, and especially those which form the foundation of further investigation, require to be fully and critically examined in order to see that the deductions drawn are justified by the facts.

3. The Field of Inquiry for the Chemist.—The aim of the chemist is then to investigate matter with a view to recognising and classifying the *essential* characters of each kind of matter, and to follow the changes which ensue whenever those changes involve a redistribution of matter.*

Let us then follow the course of investigation by experiment, which will enable us to see how the information we require is to be obtained, and what deductions may be fairly made from the observations.

Exp. 1. An apparent transmutation of iron into copper.—Into a solution of "blue vitriol" dip the bright blade of a penknife. After a short time remove the knife. Observe that the part of the blade which was immersed in the liquid has acquired the appearance of copper.

Apparently the iron of which the blade is composed has been changed into copper, and if you were to leave the investigation at this stage you might conclude that you had succeeded in bringing about a transmutation of iron into copper. Not until you have carried out an exhaustive inquiry, and performed a series of somewhat complex experiments will you be in a position to decide what is the nature of the change you have observed. And, this you are not in a position to undertake at present.

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* Whether in the operations which he performs matter may be created or destroyed must for the present remain untouched. An appeal to his later observations must decide this.

4. The Nature of Physical and Chemical Change.—At the outset of any inquiry relating to the science of chemistry it is necessary to acquire clear ideas as to the nature of chemical change and the distinction between this and physical change, and we shall find that in such an inquiry the use of the balance is indispensable.

Exp. 2.—Take the following objects:—

1. A small test-tube.
2. A porcelain crucible.
3. A few inches of platinum wire.

Weigh each of these carefully (seeing that they are quite dry and clean), and enter the weights in the column provided below, and also any notes descriptive of the objects. Now heat them for some minutes in the non-luminous flame of a Bunsen burner; observe the alterations which ensue during the heating, *e. g.* change of colour, softening, and enter these observations also in the table. In heating a crucible it will be desirable to support it on a pipe-clay triangle as shown in Fig. 1.

Allow the objects to cool, and see how far they resume their original character. Weigh them when quite cold, and enter these results alongside the others.

Weight.		Description as to Colour, Texture, etc.		
Before Heating.	After cooling.	Before Heating.	During Heating.	After Cooling.

Exp. 3.—Now perform similar experiments with the following bodies, and make observations upon them in the same way, entering all your observations in tabular form:—

4. A fragment of sulphur in a test-tube.
5. A fragment of wax in a test-tube.
6. A few crystals of iodine in a test-tube.

Carefully observe and note down any changes during the application of the heat, and also what takes place during the period of cooling. A pocket lens will be of assistance to you in some of your observations.

Do not press the heating so strongly as to drive vapours out of the mouth of the tube. [Find out, however, in the last example how it would affect the records you have made if you do so drive off vapours.]

Exp. 4.—Heat for at least fifteen minutes in small porcelain crucibles, and record your observations in the same way:

7. Some small pieces of magnesium foil (with crucible cover loosely on).
8. Some small pieces of tin (without cover).
9. „ „ wood (without cover).

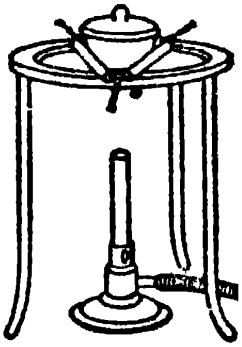

FIG. 1.

Having now before you the records of all your observations arranged in an orderly manner, you will notice that in the examples given you may collect them, *i.e.* generalise them, under the following heads:

(*a*) Those cases (1–6) in which there is no substantial* alteration of weight, and in which, though whilst the heat was being applied changes of colour, etc., may have been evident, yet on cooling, the substance had, so far as we can judge, returned to its original form and character.

While hot the test-tube softened, became out of shape, and gradually acquired a red colour, the porcelain crucible became red-hot, and the platinum wire white-hot and softer so that it could be more easily drawn asunder; but all three objects regained their original appearance on cooling, though the test-tube remained out of shape.

Again the sulphur and wax melted on heating but solidified on cooling, and then exactly resembled other fragments of the original substances; the iodine volatilised without melting, forming violet vapours, but when the test-tube was allowed to cool these vapours condensed on the sides of the tube in the form of blue-black crystals exactly like those originally taken.*

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* It will be useful to consider how very small variations having no particular bearing on the inquiry may occur, and how precautions might be taken to eliminate them.

(*b*) Those cases (7–9) in which alteration of weight (gain or loss) has taken place, and in which it will be observed that a distinct change in character and properties has been brought about.

Thus the magnesium was converted into a very light fluffy white powder and the tin into a white powder,† in both cases with gain in weight, whilst the wood gradually burned away with loss of weight.

We thus recognise a striking difference in behaviour under the action of heat. Later on we shall examine more closely into the remarkable fact that substances often gain in weight under the action of heat, for it was this which led the earlier inquirers to the conclusion that heat was a ponderable substance, and that the increase in weight was due to the addition of matter which they called "caloric" to the body which was exposed to it.

For the present, however, let us confine our attention to the cases under Exps. 2 and 3, in which no alteration of weight has been found to take place and no permanent alteration of properties.

Many familiar examples of this class of phenomena will readily occur to you. Water is well known by its appearance and character, and is presented to us commonly as rain, or collected in rivers and in the sea. In the depth of winter, however, we see it become transformed into solid ice or snow, and later changing once more into water. The inhabitant of the Arctic regions is more familiar with it as ice, and the liquid water is to him a rarity. In tropical regions the reverse is the case, ice or snow being seldom seen. Yet we can readily satisfy ourselves with the aid of the balance, that ice passes into water or water into ice without change in weight or substance. And, similarly, we may examine the relation between steam or water vapour and water itself.

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* This phenomenon (of volatilising without melting) exhibited by iodine on heating is called *sublimation*.

† Reserve these powders for a later experiment.

In the solid form it is ice or snow, in the liquid form it is water, in the gaseous form it is steam or vapour. The matter is the same, the form of its occurrence is different. That matter may exist in solid, liquid or gaseous forms and yet be in substance the same is not the exception but the rule. The difference of character is a difference of *physical state.*

Whether the substance is present to us as ice, or water, or vapour, depends on the *physical conditions* which prevail, and we realise by ordinary experience that *temperature* is the controlling factor. Yet ice may be transformed into water by *pressure* alone, or by sprinkling it with common salt.

Exp. 5.—Make a mixture of three parts by weight of snow or crushed ice and one part by weight of common salt. Stir it well together until the ice or snow is nearly all melted. Now dip into the mixture the bulb of a thermometer, and note how the quicksilver shrinks (record the lowest reading of the thermometer).

Transfer the thermometer to hot water and see how the quicksilver increases in volume, occupying a greater space than it did before. Weigh the (dried) thermometer before and after one of these operations, and show that there is no change in the mass of the glass (which also contracts and expands) and quicksilver of which the thermometer is made.

Exp. 6.—Fit a small dry flask with an india-rubber cork and glass tube of the form shown in Fig. 2, and let it dip into a vessel containing liquid. Now place the flask in the mixture of ice and salt and afterwards in hot water, and note how the air in the flask contracts or expands just as the quicksilver did, but in greater degree.

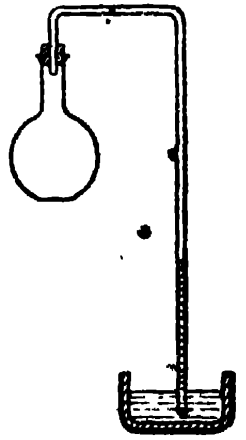

FIG. 2.

Summarising the results which these and similar observations bring home to us we find :—

(1) That matter may change in form (expand or contract), it may change in state (gaseous, liquid, solid), it may change in character (an impalpable powder, a crystalline

solid), or it may become softer or more brittle, porous or more dense, without any alteration of mass or variation of substance.

Such temporary modifications of character are classed as *physical changes.*

(2) That matter may undergo modifications in the properties which it exhibits in response to the communication from without of heat, light, electricity, which are capable of being stored up by it, but which are imponderable, and therefore likewise bring about no alteration of mass.

Such properties are termed *physical properties.*

On the other hand the permanent modifications of character which matter undergoes when its mass is altered (as in Exp. 4) are classed as *chemical changes*, and those properties of matter which it exhibits when it undergoes chemical change are termed *chemical properties.*

QUESTIONS.—CHAPTER I.

1. Briefly explain what you understand to be the *method of scientific inquiry.*
2. To what chief causes were the mistakes of the early chemists due?
3. What do you consider to be the field of inquiry for the chemist?
4. Describe an experiment illustrating the apparent transmutation of one metal into another.
5. Explain the difference between a *physical* and a *chemical* change.

CHAPTER II.

THE NATURE AND ACTION OF AIR.

5. Operations of Weighing.—Effect of Moisture.—Now let us make further inquiry into the results comprised under Exp. 4 in the previous chapter, with the view especially of learning the significance of the changes in mass which have there been recorded.

The operations of weighing must now be performed in such a manner as to secure accuracy, and exclude the complications arising from causes really external to the experiment. Vessels, and especially finely-divided substances, if left about, take up moisture from the surrounding air, and become heavier, sometimes in a marked degree. We shall simplify our labours if we proceed in such a manner as to prevent this occurring.

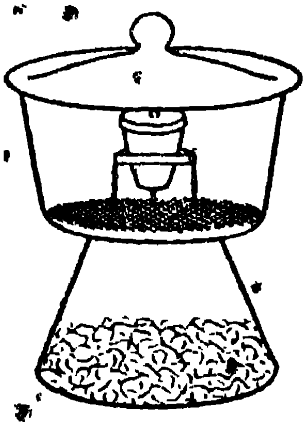
FIG. 3.

This we can do by keeping the air of the balance case as dry as possible, and by providing a dry air chamber in which to keep the vessel and substance while it is cooling, for it must never be weighed until it is quite cold. The piece of apparatus shown in Fig. 3 is termed a *desiccator*.

It is divided into two compartments communicating with one another. A circular piece of wire gauze is placed at the bottom of the upper compartment, and on this stands a pipe-clay triangle with the wires bent down to form legs;

crucibles, etc., can be supported on the triangle while cooling. The lower compartment contains calcium chloride, by means of which the air in the desiccator is kept dry.*

Exp. 7.—Take a small porcelain crucible and half fill it with finely powdered sand or dried soil. Heat it over the Bunsen burner for say fifteen minutes, till it is red-hot throughout. Now remove it at once, while still hot, to the desiccator, and allow it to cool. Weigh it as quickly as possible. Leave it in the air of the room for a day, and then weigh it again. Note the increase in weight.

We shall henceforward take it for granted that wherever accuracy is desired such precautions will be adopted in order to exclude moisture.

6. Effect of the Presence of Air.—

Exp. 8.—Introduce a small piece of lead into a porcelain crucible and weigh the whole. Heat over the flame of a Bunsen burner, and from time to time incline the crucible, turning it round so as to expose the bright surface of the metal. Continue the heating until there is no longer any bright metal to be seen, but in place of it a yellow substance, readily crushed and powdered. Cool and weigh. You will note that there is an increase in weight.

Exp. 9.—Introduce lead into a crucible as before, and then fill up with clean white sand †; weigh; heat as before without disturbing the crucible or the sand overlying the lead. After say half an hour allow it to cool, and weigh. Note that there is no change in weight. Now throw out the sand and examine the lead at the bottom of the crucible. You will find that it has undergone no change except that it has melted and solidified again. Also examine the sand and note that its appearance has not changed.

A similar pair of experiments may be made using magnesium, tin, copper, or iron instead of the lead.

In each case you will find that under the conditions of Exp. 8 the metal undergoes a permanent change in character and increases in weight, whereas under the conditions of Exp. 9 there is no permanent alteration in character and no change in weight.

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* Leave a fragment of calcium chloride on a watch glass in the air of the room, and note how in the course of the day it becomes moist and increases in weight.

† The sand should have been previously strongly heated and allowed to cool in the desiccator.

Exp. 10.—Introduce a piece of charcoal into an open crucible and weigh. Now heat the crucible and observe that soon the charcoal glows and gradually burns away, leaving only a minute quantity of white ash.

Exp. 11.—Repeat the experiment, as with the lead, covering the charcoal with a thick layer of sand. Satisfy yourself that heating, even if continued for a considerable time, fails to bring about any material alteration in the weight. Now allow the crucible to cool and turn out the contents. You will find that neither the charcoal nor the sand has undergone any change.

7. Review of the Experimental Results.—From these experiments it appears that the transformation of lead into a yellow substance, differing in mass and in properties from lead, takes place under the conditions of Exp. 8, but not under those of Exp. 9. Likewise that charcoal burns away under the conditions of Exp. 10, and not under those of Exp. 11.

In what do these conditions differ? Chemists in the seventeenth century were fully aware of these changes, and were even aware of the fact that they were accompanied by a gain (or *apparently* in some cases a loss) of mass. The increment of substance was, however, regarded for long as of small importance, and attributed to particles derived from the flame.

In these experiments the flame and the heat are provided under both sets of conditions, and the sole difference that can be detected is that in one case there is free access of air, whilst in the other the substance is imprisoned beneath the sand and shut off from the air.

8. Action of Air during the Heating Operation.—Before we proceed to examine how and why the air effects such a change, let us satisfy ourselves that the lead, however unlikely it may appear to be so, is still contained in the yellowish residue from Exp. 8.

Exp. 12.—Scrape out of the crucible some of this residue, powder it very fine, and introduce it into a fresh crucible. Now take about a gramme of finely-powdered charcoal, and mix it (by stirring with a thin glass rod) intimately with the yellowish powder. By gently tapping the crucible shake the contents well together, and cover the surface with a layer of powdered charcoal. Put a lid on the crucible.

[Why?] Heat over the flame for an hour without disturbance. Allow to cool, and then carefully shake out the charcoal and see what lies under it.

Examine the substance, press it in a mortar, and satisfy yourself that it corresponds to the metal taken in Exp. 8.

The suggestion which these experiments give rise to, that air plays an important part in the changes observed, is one that must be tested with great care, and further experiments must be devised in order more fully to appreciate the nature of the changes. For the present you will be satisfied to note, that while heating in air transformed the lead into a yellow powder with increase in mass, the heating of this yellow powder with charcoal has brought it back to metallic lead again.

9. The changes which Air may effect at Ordinary Temperatures.—Rusting of Iron.—Our next investigations will be made upon *iron*, a substance which possesses the advantages of being familiar to us, not only in itself but in the changes which it undergoes, and also in respect of the fact that such changes take place at ordinary temperatures.

Exp. 13.—Obtain some bright iron or steel filings,* sprinkle a thin layer of them on a watch glass; weigh; place in the desiccator, and leave them there for two or three days, after which again weigh. You will find that the weight remains unaltered. Examine the filings with a lens; they present the same appearance as at first.

Exp. 14.—Perform the same operations with the difference that the filings are left under a bell-jar, the inner surface of which is well moistened with water. This time you will find that there is an increase in weight and that the filings have become covered more or less completely with a reddish-yellow powdery-looking substance.†

The change which has taken place in the one case, and of which evidence is wanting in the other, is one that you must frequently have observed in iron utensils, railway lines, etc. It is termed "rusting," and the reddish-yellow powder formed is called "rust." So far you find it to be

* Such filings are usually contaminated with oil, and this should be removed by shaking them with a little *ether*, pouring off the liquid, and then leaving them a few minutes in a dry, warm place—in a steam bath or in a gently warmed basin.

† Reserve these rusty filings for a later experiment.

associated with an increase in weight and apparently due in some way to the moisture, for in dry air it did not take place. Let us now try to find out whether rusting will take place in the presence of *moisture alone*.

Exp. 15.—Fit a round-bottomed flask of about a litre capacity with a rubber cork, through which passes a short length of rather wide glass tubing to which is attached an inch or two of indiarubber tubing. Introduce about 300 c.c. of hot water, and drop into this some yards of bright iron wire wrapped into small compass by winding it round the fingers. Now boil the water, not too violently, but so that the steam issues freely from the end of the rubber tubing. Continue the boiling for at least a quarter of an hour, and then slip over the rubber tubing a strong brass clip, being careful, *just the instant before doing so*, to remove the burner. During the boiling the steam will have displaced the air almost completely from the flask. By turning the flask about you will be able to expose the wire to the space occupied by water vapour. Leave it so for some days, and note that the wire keeps quite untarnished. After that let in air, and notice how after some hours reddish-yellow rust forms on the wire.

The rusting of the iron therefore takes place only in presence of air and moisture, and does not occur either in *dry* air or moisture alone.

10. Does all the Air take part in the Process?

Exp. 16.—Take now a tall narrow cylinder moistened over its inner surface, and sprinkle iron filings freely over this surface. Invert over water contained in an earthenware or glass trough, taking care that you do not let any air escape from the cylinder. Note that soon the water begins to rise in the cylinder, and that after a day or two it rises no further. The air in the cylinder is now under diminished pressure. To restore the pressure to that of the atmosphere pour water into the trough till the level is the same inside and outside the cylinder. Mark the level carefully by means of a piece of gummed paper. Now remove the cylinder, empty it, and pour water into it from a graduated cylinder, noting the volume of water needed—

(*a*) To fill up to the mark.

(*b*) To fill it from the mark to the top.

You will find that the ratio $a : b$ is approximately 4 : 1.

Repeat the experiment, and if in the first experiment none of the filings remained bright after the water had ceased to rise, use a quantity sufficiently large for this to be the case. You will find that the result is the same.

Obviously then only about one-fifth of the air takes part in the process of rusting, for some of the filings remain bright after this quantity has been removed.

11. What has become of the Air which has disappeared?—Recalling the fact demonstrated in Exp. 14 that the rusting of iron is accompanied by an increase in weight,* we are justified in concluding that the air which has disappeared has become in some way fixed or added on to the iron, and that the result of this fixation is the conversion of the iron into reddish-yellow rust.

12. The Nature of the Change which takes place when Metals are heated in Air.—We have seen in Exps. 4 and 8 that when metals are heated in air they increase in weight and become changed into earthy-looking powders (which the early chemists called "calces" [sing. "calx"] of the metals). Can we explain these changes as we did the rusting of iron? If so, then they should be accompanied by the disappearance of a certain amount of air. Let us test this by burning magnesium (for example) in an enclosed volume of air.

Exp. 17.—Arrange a bell-jar in a trough containing water (see Fig. 4). Let the bell-jar be ground on the base, and be not too narrow nor too large. If the trough be a glass one, it will be necessary to have a thin disc of rubber on the bottom upon which to press the bell-jar firmly and so prevent any escape of air through expansion by the heat of combustion. Mark the level of the water in the jar by means of a piece of gummed paper. Attach a piece of magnesium ribbon to a cork which fits the bell-jar well. Ignite the magnesium, and *as quickly as possible* place it in the bell-jar, pressing down the bell-jar firmly with the other hand, and pushing in the cork tight. After burning brightly a short time the magnesium goes out. The water rises rapidly inside the jar. When it ceases to rise further pour water into the trough till the level is the same in bell-jar and trough. Again mark the level of the water with gummed paper. Now proceed, as in Exp. 16, to measure the volume up to each gummed mark. The larger volume (say v) represents the volume of air originally present in the jar; the difference between the two (say $v - v_1$) the volume of air which has disappeared. You will find that $v - v_1 : v = 1 : 5$, *i. e.* one-fifth of the air has disappeared as in Exp. 16.

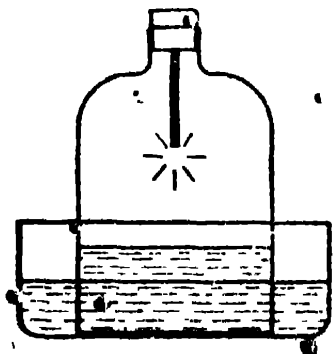
FIG. 4.

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* It is assumed that the student is acquainted with the fact that *air has weight.*

Similar results would be obtained by heating other metals in an enclosed volume of air, so that we may safely conclude that the change in appearance and properties and the increase in weight which the metals undergo is due to the fixation of air on them.

Exp. 18.—Allow some iron to rust in a cylinder of air, as in Exp. 16, till the level of water ceases to rise. Place a glass plate over the mouth of the cylinder, take it out of the water and stand it upright on the table. Remove the glass plate and introduce a lighted taper; it is extinguished. Next burn magnesium in a bell-jar, as in Exp. 17. Now take the cork out of the jar and introduce a lighted taper; again it is extinguished.

From this similarity in behaviour, and from the fact that in both Exps. 16 and 17 about one-fifth of the air was removed, we may suppose that ordinary air consists of two gases in the proportion of 4 : 1 by volume, and that iron on rusting and magnesium on burning have removed the constituent present in smaller quantity. This we may term the *active constituent*, and that present in larger quantity the *inactive constituent*. The latter has been named *Nitrogen*, and we shall in future call it by that name.

13. **Burning of Non-metallic Substances in Air.**—Metals are, however, not the only substances which will remove the active constituent from air; any substance which will burn in air is capable of doing this, *e.g.* phosphorus, sulphur, a candle. Let us demonstrate this in the case of the first-named substance.

Exp. 19.—Stand a small porcelain crucible containing some red phosphorus on a cork, and float on water in a trough. Place a large bell-jar with a narrow neck over the crucible. Mark the level of the water in the jar with gummed paper. Now ignite the phosphorus by touching it with a hot wire, and close the bell-jar *at once* by means of a cork or stopper. The phosphorus will burn brightly at first, and the heat evolved will expand the gas and depress the water inside the jar. After a little time the combustion will cease, and the water will ultimately rise above its original level. The fine white powder which is formed during the combustion (consisting of phosphorus pentoxide) will gradually settle down, and dissolve in the water. When the water has ceased to rise within the jar, pour more water into the vessel in which it stands until the level is the same in both. You will find (using the method of Exp. 16) that *one-fifth of the air* has disappeared. Test the residual gas as in Exp. 18. It is nitrogen.

Note.—Burn away all the remains of phosphorus in the crucible in a fume cupboard; *do not wipe it off with a cloth.*

14. The Active Constituent of Air (Oxygen).—We must now inquire whether it is possible to recover the active constituent of the air from the calx of a metal.

We choose for our first experiment a calx of mercury known as "red precipitate," and which can be obtained by heating mercury for a long time at a certain temperature in contact with air.*

Exp. 20.—Into a hard-glass tube introduce sufficient crystalline red precipitate to cover a threepenny-piece, and hold it in a Bunsen flame. Notice that the colour of the powder changes from scarlet to black—it looks "*burnt.*" Take the tube from the flame, let it cool, and notice what happens. The scarlet colour is recovered. Evidently the change is not due to *burning.*

Have by you a splinter of wood long enough to reach down to the bottom of the tube. Now heat the latter in the hottest part of the flame (*i.e.* near the tip). You will observe a mirror gradually forming on the sides of the tube. Ignite the splinter, blow out the flame, and thrust the glowing end down the tube. Observe that the glowing splinter bursts into flame, and burns more brightly than in common air.

Now scrape off the mirror formed in the tube with the clean end of the splint. You obtain a liquid metallic globule of "quicksilver" or *mercury.*

If, then, mercury is heated in air to a certain temperature, we obtain the calx of the metal; and we have just found that, by heating the calx to a *higher temperature* (for the temperature of the hottest part of the Bunsen flame is much higher than that at which mercury is converted into red precipitate), the calx has been broken up again into mercury and a gas which is more active than ordinary air. This gas must, therefore, be the active constituent of air. It is called *oxygen.*

Exp. 20 (*continued*).—Try the same experiment, using red lead. Here, again, you obtain oxygen; *but the residue in the tube is not metallic lead:* it is a yellow solid, litharge, which is the *yellow* calx of lead, that is, the substance obtained in Exp. 8 by heating lead in air. [Red lead is also obtained by heating lead in air, but a lower temperature must be used than in the preparation of litharge.]

Now heat in a similar way the white powders you obtained from magnesium and tin in Exp. 4, and the rusty iron filings formed in Exp. 14. None of these gives off any oxygen.

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* Red precipitate is usually prepared by quite a different method, and is a substance which may be easily procured from the chemist.

It is clear, therefore, that the oxygen is not recoverable from *all* the bodies obtained by heating metals in the air or simply exposing them to the air, as in the case of iron rust—at any rate, not by simple heating.

15. **Elements and Compounds.**—Red precipitate contains, then, at least two substances—mercury and oxygen—which are joined together in some mysterious way, so that the product is an entirely different substance from either of its constituents. This kind of union is termed *chemical combination*, and both the formation of this substance by heating mercury in air and its subsequent decomposition by heat are excellent examples of *chemical changes*. Red precipitate is an instance of a chemical compound; so also are red lead, iron rust, and the calces of the metals in general. Chemical compounds, then, are evidently substances which may be split up into two (or more) new substances. Now neither mercury nor oxygen has, so far, by any means in the chemist's power, been decomposed into anything simpler. Substances like mercury and oxygen, which have up to the present resisted all attempts to break them up into simpler bodies, are termed **elements**. Nitrogen is also an element, as are all the pure metals, as well as sulphur, carbon, and a great many substances. In all about 75 elements are known; but some of them are very rare, and only obtained with great difficulty.

A chemical compound containing oxygen and some other element is termed an *oxide:* red precipitate, for instance, is *oxide of mercury;* red lead and litharge are *oxides of lead;* iron rust is an *oxide of iron.*[*]

16. **Preparation of Oxygen in Quantity.**—We have seen that it is not easy to obtain supplies of pure oxygen, unmixed with other gases, from the atmosphere; nor are there naturally occurring substances which readily yield the gas in quantity. "Nitre," which is found in quantity in Chili, and "pyrolusite" (manganese dioxide) will, when *strongly* heated, give up fire-air, and were used by the earlier chemists as sources of the gas.

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[*] It is not, however, pure oxide of iron; in addition it contains ferric hydroxide and ferrous carbonate in varying proportions.

There are, however, substances which have been specially prepared by the chemist more convenient for the purpose than red precipitate, or red lead, or any of these naturally occurring bodies. One of these is "chlorate of potash," the nature of which you will more fully appreciate at a later stage. We shall use it at present merely as a means of obtaining oxygen free from other gases.

Exp. 21.—Heat a small quantity of potassium chlorate in a test-tube. Notice that it first crackles, then melts, and at last seems to boil. At this stage test the issuing gas with a glowing splinter. It will be found to be oxygen. Now heat some more potassium chlorate, first grinding it up in a mortar with a little manganese dioxide, till the substances are thoroughly mixed. Observe that the mixture gives off oxygen much more readily than potassium chlorate alone.

It is a remarkable fact that the manganese dioxide is unchanged at the end of the operation, the oxygen appearing to have come from the chlorate only. It is, however, very likely that the manganese dioxide does take part in the reaction, but we cannot stop to discuss the question here.

The mixture just described is the one generally used to prepare oxygen in large quantities, and is often called the "oxygen mixture."

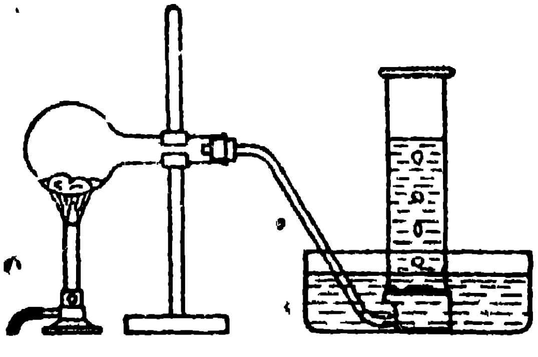

Fig. 5.

Exp. 22.—Procure a small round-bottomed flask of hard glass, and fit it with a cork and delivery tube bent as shown in Fig. 5.

Pour sufficient water into a pneumatic trough to cover its shelf by at least half-an-inch. Fill one large gas-jar and five smaller ones with water and invert them in the trough. Have ready some ground-glass covers to be placed over the mouths of the jars when filled with gas.

Fill the flask about one-quarter full with a mixture of potassium chlorate with about one-quarter of its weight of manganese dioxide,

and fix it as shown in the figure,* so that the delivery tube just dips under the shelf of the trough. Use a small flame to heat the mixture, and move it to and fro to avoid getting too high a temperature. Oxygen soon comes off rapidly, and after allowing a short time for the air in the flask to be driven out, place a jar in position on the shelf, and, when filled, quickly cover its mouth while still under water with a glass plate, and replace it by a second jar, and so on.

We have collected the oxygen by the "displacement of water," a method generally employed for collecting gases that are not too soluble in water.

Note on Manganese Dioxide.—Before using a fresh sample of this compound for the production of oxygen, it should always be tested for carbonaceous matter (soot, etc.), as such material is apt to cause explosion when heated with potassium chlorate. To do this, mix it with some of the chlorate and heat gently in an open crucible. If the action is violent, reject the sample of dioxide.

17. Properties of Oxygen and Comparison with Ordinary Air.—

Exp. 23.—You will already have noticed that oxygen is colourless like ordinary air. Remove the cover from a small jar of the gas and inhale a little of it. You will find that it is odourless and tasteless, but that it produces a feeling of exhilaration as though it were ordinary air *intensified.*

Exp. 24.—Fill the bowls of two deflagrating spoons (see Fig. 6) with flowers of sulphur, ignite the sulphur and plunge one spoon into a jar of air, the other into a small jar of oxygen, taking care that the brass plates of the spoons fit down on the jars. Observe that in both cases the sulphur burns with a pale blue flame and gives off white fumes, and that on slightly raising the spoons the familiar disagreeable odour of burning sulphur is noticeable. The only difference you will observe is that in the case of oxygen the burning is more vigorous and the smell more intense.

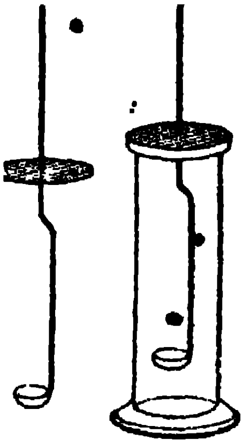

FIG. 6.

Note.—Burn off all the sulphur remaining on the spoon before doing the next experiment.

*** The mixture is almost certain to contain adhering moisture which would be driven off on heating and condense in the neck of the flask. If, therefore, the flask is supported in a vertical position there is a danger that this moisture would run down on to the hot part of the flask and crack it.**

Exp. 25.—Cut off from some yellow phosphorus, *held below water*, a piece not bigger than a pea, and transfer it on the point of a knife to the clean, cold deflagrating spoon. Dry it by touching it with a bit of filter paper, and watch it for a few seconds. White fumes with a peculiar odour are given off; the phosphorus is already reacting with the air. Touch the phosphorus with a warm glass rod and plunge it into a jar of air, keeping the brass plate well down on the jar. Note that the phosphorus burns with a bright white flame evolving dense white fumes.

Repeat the experiment with a small jar of oxygen and observe that the result is the same, but that the flame is more brilliant.

Note.—Burn away all the remains of phosphorus on the spoon in a fume cupboard.

Exp. 26.—Wire a bit of charcoal to the end of a deflagrating spoon. Make it red-hot, then remove it from the flame and watch it. It soon ceases to glow. Now make it red-hot again and introduce it into a small jar of oxygen. It continues to glow and gradually disappears, just as it did in air when the external heating was kept up as in Exp. 10.

Exp. 27.—Attach a piece of magnesium ribbon to a deflagrating spoon, ignite the end of the ribbon and plunge it into a jar of air. Note that the magnesium burns with a very bright flame and formation of white fumes, which settle down as a white powder on the walls of the jar. Repeat the experiment with a small cylinder of oxygen. You will observe that the result is similar but that the burning is much more vigorous, the flames being intensely bright.

Exp. 28.—Introduce through a funnel sufficient sand to cover the bottom of the large jar of oxygen which you collected to a depth of about half-an-inch. Roll 8 or 10 inches of thin iron wire round a glass rod to form a spiral, and fasten a bit of match stalk to one end. Attach the other end to a deflagrating spoon. Light the match and plunge the wire into the jar. The iron wire burns and small black globules fall on to the sand. Repeat this experiment, using a cylinder of air; the wire does not burn.

It is quite obvious from the foregoing experiments that oxygen possesses the properties of ordinary air in an intensified degree, or in other words that air behaves as though it were diluted oxygen. We shall experience no difficulty in understanding this when we recall the fact that only one-fifth of the air is oxygen, the remainder consisting of the inactive gas nitrogen.

QUESTIONS.—CHAPTER II.

1. Describe a *desiccator* and explain its use.
2. Describe two experiments illustrating the part played by air in chemical changes. [illegible]
3. What conditions are necessary for the rusting of iron? Describe experiments in support of your answer.
4. What do you suppose takes place when magnesium burns in air? Describe the experiments you would perform to verify your statement.
5. What is red precipitate? What happens when it is heated? What other red powder behaves somewhat similarly? In what respects do they differ?
6. Distinguish between "element" and "compound." Give as many examples as you can of substances belonging to each of these classes of bodies.
7. How would you prepare oxygen gas in quantity? Sketch the apparatus you would use. Describe in detail the experiments you would perform to show that when substances are burnt in oxygen, the products are the same as when the same substances are burnt in air. [illegible] + $2KClO_3 \rightarrow 2KCl + $ [illegible]
8. Describe as carefully as you can how you would prove that when phosphorus burns in air in a confined space one-fifth of the air disappears. What has become of this portion? Why is it necessary to make the level of the water inside and outside the jar the same before measuring the residual volume of air?

CHAPTER III.

THE NATURE AND ACTION OF WATER.

18. **Behaviour of Substances towards Water.**—We will commence our study of water in a manner similar to that which we followed in the case of air, *i. e.* by investigating the changes which familiar substances undergo in contact with water. Let us take *nitre* or *saltpetre* (potassium nitrate) as our first substance.

Exp. 29.—In a test-tube containing a little cold water place a few crystals of nitre. Notice that they gradually get less and less in bulk, and finally disappear *from sight*. We say the nitre has dissolved, and that it is *soluble* in water. What we have in the test-tube now is a *solution of nitre in water*. The water is termed the *solvent*. The word *solute* has been suggested for the substance (in this case nitre) that has dissolved.

Now add more nitre, and shake; probably that will dissolve also. At length, however, if we continue to add the solid, a point will be reached at which some will remain undissolved in that quantity of water.

We have now a *saturated solution* of nitre in *cold* water. There are two ways in which we could cause the still undissolved portion to pass into solution: one is very obvious —namely, the addition of more water; the other, not so obvious, is by warming the water already there. The hot solution would dissolve more nitrate before the point of saturation was reached; but *this* also would, in the end, become saturated. We may obviously have saturated solutions at various temperatures, and it is evident that the quantity of solid necessary to produce such a solution will depend on two things at least—(1) the quantity of water present; (2) the temperature of that water.

19. Crystallisation.—If now the hot saturated solution be allowed to stand for some time, the nitre will reappear; it will separate out from the solution in the form of crystals, but only in part; for the remaining liquid must always be a saturated solution. These crystals will almost certainly be large and well formed, as crystals usually are when they form by the slow cooling of hot saturated solutions (or the slow evaporation of cold saturated solutions).

Exp. 29 (*continued*).—Allow the hot solution of nitre to stand. Note the formation of crystals.

If the hot solution be poured into a clock-glass, the crystals will be small and will separate more quickly, because the cooling is rapid owing to the large surface exposed. A crystal has a definite geometrical form, and many substances may be recognised by the shape of their crystals. The student should examine and draw well-formed crystals of calcite, alum, sugar, and blue vitriol. If a well-formed crystal of any substance be suspended by a very fine thread in a saturated solution of the same substance, it will grow at the expense of the solution, but will usually retain its shape. In this way very large and almost perfect crystals of some substances may be obtained. Alum is a good substance to experiment with in this way.

Water of Crystallisation.—Many crystals when heated give off water and fall to a powder. Blue vitriol, or copper sulphate, will serve to illustrate the peculiarity of some crystalline substances.

Exp. 30.—Grind up some crystals of copper sulphate to a fine powder. Introduce a little of the powder into a porcelain crucible and weigh (with lid). Place the lid so that it only partly covers the crucible, and heat over a small flame which does not touch the crucible. Notice that the powder gradually becomes white. Now place the lid completely on the crucible and remove to a desiccator. When cold weigh. You will find that there is a loss in weight.

Now drop a little water upon the powder (anhydrous* copper sulphate) and note the return of the blue colour. This serves as a delicate test for the presence of water.

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* From a Greek word meaning *without water*.

If the white powder is dissolved up again in water and partially evaporated, and then set aside to cool, blue crystals may again be obtained. Water appears to be essential to the formation of some crystals. Such water is termed *water of crystallisation.* Washing soda, alum, and borax contain also a large proportion of such water.

Amorphous substances are those which do not possess a crystalline form. Examples of this class are chalk, charcoal, and starch.

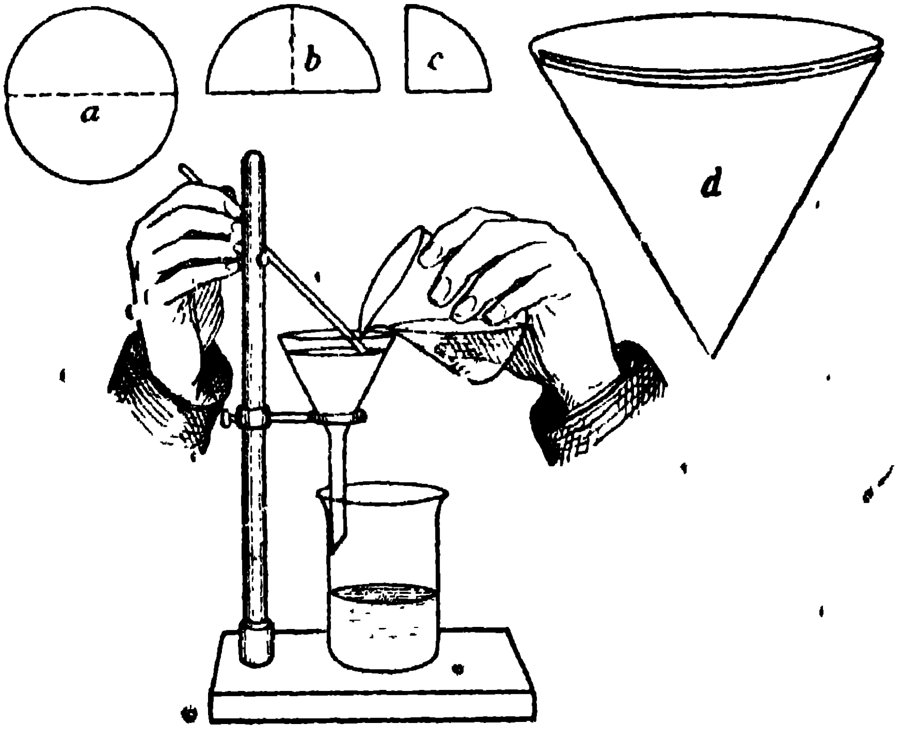

FIG. 7.—*a, b, c, d* indicate the manner of folding the circular filter paper.

20. Filtration.

Exp. 31.—Fit up a filter of the form shown in Fig. 7, and pour through it some of the nitre solution obtained in Exp. 29 (using unglazed paper, called *filter paper*). You will find that the whole of it runs through. Nothing of a solid character is retained by the paper.

From this we gather that *dissolved matter cannot be removed by filtration*; the pores of the filter paper are evidently larger than the particles of the dissolved substance (as well as those of the solvent). To recover the ***solute*** (nitre in this case) we must either boil off the solvent (water) or allow it to evaporate into the air.

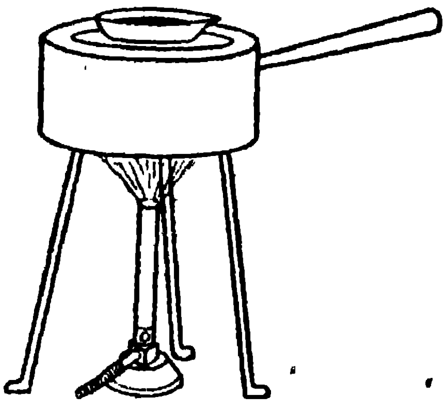

Fig. 8.

Exp. 31 (*continued*).—Pour some of the nitre solution into a porcelain dish and evaporate off the water by placing it on a water bath (see Fig. 8) The nitre remains behind.

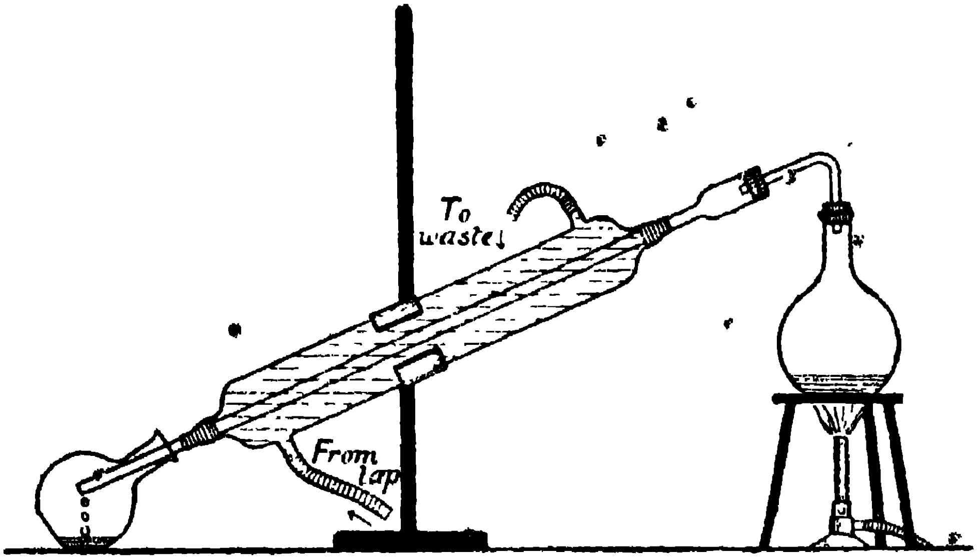

Fig. 9.

Distillation.—If we wish to recover the ***solvent*** (in this case water) we must make suitable arrangements to condense it. This is best done by using a ***Liebig condenser***, which consists of a glass tube surrounded by a wider tube, through which cold water is made to circulate (Fig. 9).

Exp. 31 (*continued*).—Pour the remainder of the nitre solution into a flask and connect with a condenser, as shown in Fig. 9. Boil the liquid in the flask. The steam passes through the inner tube of the condenser, where it becomes liquid, and flows down into the flask placed to receive it. Do not boil off all the water or the flask may crack. Evaporate to dryness a little of the condensed liquid. There is no residue, shewing that only the water has passed over.

The process of boiling a liquid and condensing and collecting the vapour as you have done in Exp. 31 is known as *distillation*.

21. **Solubility Curves.**—Let us now investigate the solubility of nitre quantitatively at different temperatures.

Exp. 32.—Introduce about 100 c.cs. of water into a small flask, add some finely powdered* nitre, and shake well. If the powder all dissolves add more and shake again. Repeat the addition of nitre, if necessary, till some remains undissolved after vigorous shaking, *i. e.* the solution is *saturated.* Allow the mixture to settle, take the temperature of the liquid with a thermometer (say 10° C.), and then pour off about 10 c.cs. of the clear liquid into a weighed porcelain dish, after carefully wiping the inside of the neck of the flask, on which there may be some solid nitre, or water unsaturated with nitre. Weigh again. The difference gives the weight of the solution (w gms. say).

Now evaporate to dryness on the water bath, wipe the moisture off the bottom of the dish, and weigh. The difference between this and the weight of the empty basin gives the weight of nitre dissolved.

Suppose this is w_1 gms., then we have w_1 gms. of nitre dissolved in $w - w_1$ gms. of water. Therefore at 10° C. the weight of nitre which would dissolve in 100 gms. of water would be $\frac{w_1}{w - w_1} \times 100$ gms. This is the *solubility of nitre at* 10° C. *expressed as a percentage.*

Now warm the water in the flask to about 20° C. and find the solubility as before. Repeat at 30°, 40°, and 50° C.

Next take a piece of squared paper and draw two lines (axes) at right angles, one horizontal along the bottom of the paper, the other vertical along the left-hand side.

Mark off along the horizontal axis lengths proportional to the temperatures taken, and on the vertical axis lengths proportional to the solubilities. Now from each point representing a solubility draw a horizontal line till it cuts a vertical line from the corresponding temperature. Make a cross at the point of intersection. Join the centres of the crosses by a line, drawing the line so that it forms a smooth curve (see Fig. 10). This is called the *solubility curve* of nitre.

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* Solution takes place more rapidly and effectively if the substance is finely powdered.

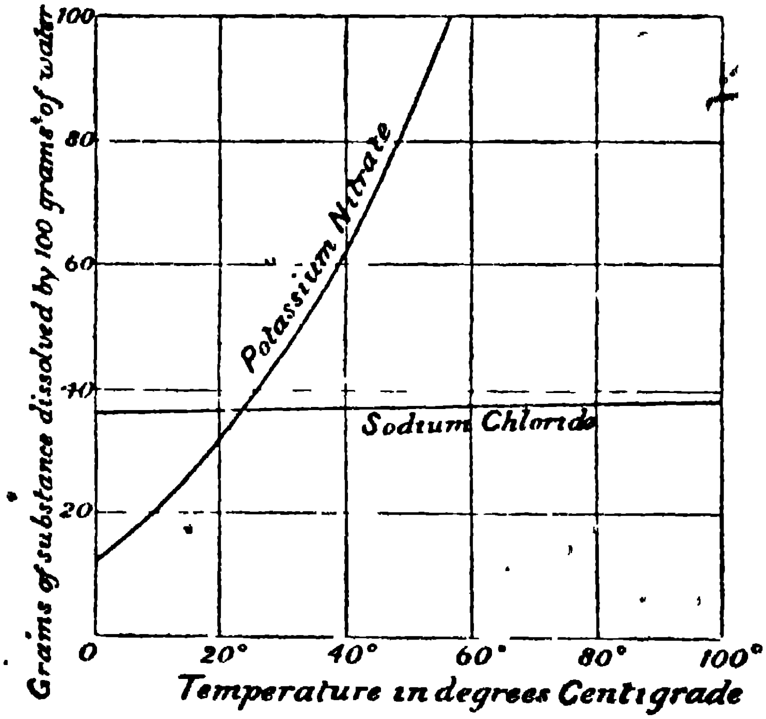

FIG. 10.

By means of this curve you can at once find the solubility of nitre at any temperature between 0° C. and 50° C. All you have to do is to follow the vertical line corresponding to the required temperature till it cuts the curve; then follow the horizontal line from this point till it cuts the vertical axis and read off the solubility.

Other examples of soluble substances are common salt, sugar, Epsom salts, bicarbonate of soda, alum and borax. You might construct solubility curves for them as you did for nitre. You would find that the solubilities of these substances vary greatly; also that whilst in some cases, *e.g.* nitre, the solubility increases very rapidly with rise in temperature, in other cases, *e.g.* common salt, the increase is very slight indeed.

22. Other Solvents.—It is important for the student to remember that water is not the only substance which possesses this property of dissolving solids. *All* liquids possess this power, in a greater or less degree, though any given liquid does not necessarily dissolve the same substances as another liquid.

Some substances that will not dissolve in water dissolve readily in other liquids. Sulphur, for example, is very soluble in a liquid called *carbon bisulphide*, and resin in *alcohol* or *methylated spirit.*[*]

Exp. 33.—Powder a small piece of sulphur and introduce it into a little carbon bisulphide in a test-tube, a little at a time, and shake till completely dissolved. Then pour on to a clock-glass and allow the liquid to evaporate slowly (in a fume closet). Note the yellow crystals of sulphur which form.

23. Insoluble Substances.—

Behaviour of Chalk towards Water.—

Exp. 34.—Shake up a quantity of chalk with distilled[†] water and allow the mixture to stand for a considerable time; the chalk settles down to the bottom, and leaves a clear liquid above. A quantity of this clear liquid may be poured off (*decanted*) without allowing any chalk to be carried with it. Substances which have a greater density than chalk (such as red lead) would subside sooner, and the liquid above could in those cases be more easily and completely separated from the solid.

This is the process known as *separation by decantation.* We could never by this means effect complete separation. We could, however, separate the chalk and water quite easily and completely by means of the filter described in § 20.

Exp. 34 (*continued*).—Pour the mixture of chalk and water on to a filter. The liquid portion which runs through the filter is termed the *filtrate*, and the chalk left on the paper is called the *residue.*

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[*] These liquids are very volatile and inflammable, and should not be boiled in the open air, but in a distillation apparatus, on a water-bath. They may, however, be allowed to evaporate slowly in the open air, without the application of heat.

[†] *Distilled water* is water produced by boiling ordinary tap water and condensing the steam by a suitable cooling apparatus; on the small scale a Liebig condenser (see Fig. 9) may be used for this purpose. Distilled water contains no dissolved solid matter.

It remains to be seen *whether the filtrate contains any chalk in solution.* To ascertain this, evaporate some to dryness on the water bath. *No residue is left;* hence we conclude that chalk does not dissolve in water.

The experiment should now be repeated with gypsum and slaked lime, and the results compared. Both these substances will be found to dissolve, but only to a slight extent.

Since the chalk is retained by the filter paper, it is evident that the pores of the paper are too small to allow the chalk particles to get through, but they cannot prevent the water passing through, nor were they small enough to prevent dissolved nitre going through with the water.

The residue on the filter paper may be dried by heating at some distance over a small Bunsen flame, or in a steam oven, and by this means recovered in its original form.

Substances which do not dissolve in water, but which when mixed with it, even in small quantity, can still be seen, are said to be *suspended* or *in suspension. Suspended matter* can always be *completely removed by filtration*, provided the filter paper is fine enough.

Sulphur, red lead, sand, charcoal, may be mentioned as other examples of bodies which are insoluble in water.

24. **Separation of Mixtures.**—It will not be difficult now for the student to see how we could effect a separation of two substances when one is soluble in some liquid and the other is not. It is only necessary to warm the mixture gently with an excess of the solvent, and filter. The insoluble portion remains on the filter, the soluble portion runs through and may be recovered as described already (by evaporation of the solvent). Chalk and nitre should now be mixed, and the substances separated in the way just described.

Exp. 35a—Separation and Isolation of the Constituents of Gunpowder.—Using the knowledge already gained concerning soluble and insoluble substances, the student will find this also an instructive exercise. Gunpowder contains three ingredients—nitre, sulphur, and charcoal. Of these nitre is soluble in water; sulphur and charcoal are insoluble; but of these sulphur dissolves in carbon bisulphide

To separate them we proceed as follows:—Shake the gunpowder with water, warm gently, and filter: the filtrate contains the nitre, which can be recovered by evaporation of the water; wash the residue on the filter by pouring water over it a few times, then dry it carefully; scrape it off the paper and add carbon bisulphide. Shake and allow to stand; filter off the liquid from the black charcoal and let it evaporate slowly in a fume cupboard. The sulphur is thus recovered. The charcoal remains behind on the filter. It should be washed with a little carbon bisulphide to free it from adhering sulphur, and then dried.

25. **Water as a Solvent for Liquids.**—Water dissolves not only many solids, but also some liquids as well. If alcohol is shaken up with water, the two liquids mix thoroughly, and no process of filtering will separate them. Every one, on the other hand, is familiar with the behaviour of oils towards water. Oils do not dissolve in water, but either float on the top or sink to the bottom, according as their density is less or greater than that of water. Partial separation may be effected in these cases by decantation; but for more complete separation we must have recourse to special apparatus (such as the separation funnel).

Carbon bisulphide, chloroform, and turpentine are other examples of liquids which do not dissolve in water: the first two, being denser, sink; the last-named, being lighter, floats on the water. Ether is an example of a liquid which is only slightly soluble in water; so that some would dissolve while the remainder would float on the water.

26. **Water as a Solvent for Gases.**—When a bottle of soda water is opened, bubbles are seen to rise in large quantities to the surface. When these bubbles have ceased coming off the liquid can be made to effervesce again by shaking the bottle. When shaking no longer produces effervescence, a further supply of bubbles can be liberated by warming the liquid. All this effervescence is due to the escape of *a gas that was dissolved in the water.* By means of a suitable arrangement this gas, which is carbon dioxide, can be collected.

Again, ordinary tap water contains gas dissolved in it.

This gas consists of air and carbon dioxide;* it may be partially expelled on warming the water, and may be completely expelled on heating to the boiling point. Unlike solids, *gases dissolve better in cold water than hot.* The quantity of a gas dissolved in water will depend upon the pressure exerted by the gas upon the water, as well as upon the temperature of the water. The gas in soda water is forced in under pressure; when the pressure is relieved by taking out the stopper some of the gas escapes.

One litre of ordinary water at 15° is able to dissolve at the ordinary pressure about 16 c.c. of air.

Aquatic animals (fishes, etc.) obtain the air they breathe from that which is dissolved in the water in which they live.

Just as in the case of solids and liquids, some gases dissolve more readily than others. It is especially important to remember in some of the experiments that follow that water is able to take up gases if brought in contact with them.

QUESTIONS.—CHAPTER III.

1. Explain the terms *solvent, solution, water of crystallisation, saturated solution.* How would you separate and recover the ingredients in a mixture of powdered sulphur and common salt?
2. Describe carefully how you would proceed to ascertain whether a given white powder was soluble in water or not. How would you expect the following substances to behave when added to water:—Epsom salts, powdered charcoal, carbonate of soda?
3. Describe in detail how you would proceed to obtain pure water and pure nitre from a solution of nitre in water. Sketch the apparatus you would employ.

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* Tap water always contains a considerable quantity of carbonic acid gas derived from subterranean sources.

4. What do you understand by the term *solubility curve*? How would you proceed experimentally to obtain the solubility curve of washing soda between 15° C. and 70° C.?
5. How would you proceed to prove that alum is more soluble in hot than in cold water?
6. Explain what is meant by *distillation*, and describe an experiment to illustrate its use.
7. Describe how you would proceed to investigate the action of heat on blue vitriol. State and explain what you would observe.
8. If you were provided with a mixture of chalk and powdered borax, how would you proceed to obtain a pure dry specimen of each constituent?

CHAPTER IV.

THE NATURE AND ACTION OF WATER (*Continued*).

27. Action of Water on Metals.—Production of Hydrogen.—

(a) Sodium.

Exp. 36.—Take a piece of sodium about the size of a pea (*not larger*) and drop it into a small quantity of water contained in a beaker. Watch the behaviour of the metal through the *side* of the vessel, not over it, as the hissing globule sometimes explodes. A thin heavy stream may be seen falling from the disappearing metal. Is the metal simply dissolving in the water? It was angular when cast on the water: it is now globular; the solid has become liquid. Its temperature has probably risen. Had the metal been placed upon a floating filter paper, the temperature would have risen sufficiently to produce a flame. Chemical action between the metal and the water may therefore be suspected.

Fill a small gas-jar with water and invert it in a trough. Cut off a piece of sodium about the same size as the first, wrap it up in tin-foil or thin sheet lead perforated with a few pinholes, and place it under the gas-jar. Bubbles of gas are now seen to rise apparently from the metal. When bubbles cease to rise place a greased cover over the mouth of the jar and turn up the latter. Bring a lighted match near and slide the cover to one side. The gas burns with a yellow flame.

The inflammable gas is called hydrogen. The yellow colour of the flame is due to the sodium.

Rub the liquid in the beaker between your fingers. It is soapy. Taste it. It is *caustic*. Test it with red litmus paper.* The colour changes to blue; *i. e.* the solution is *alkaline*. Evaporate the liquid to dryness in a porcelain dish. The residue is not sodium, which we should expect to find if the metal had merely dissolved in the water. The white solid is *caustic soda*, and is the same substance as that from which the solution labelled "sodium hydroxide" is made. Dilute a few drops of this liquid with water and apply the tests to it mentioned above.

(*b*) *Iron.*

We have seen in Exp. 15 that water alone has no action on iron even at the boiling point.

Let us now try whether there is any action at a higher temperature, namely at a red heat.

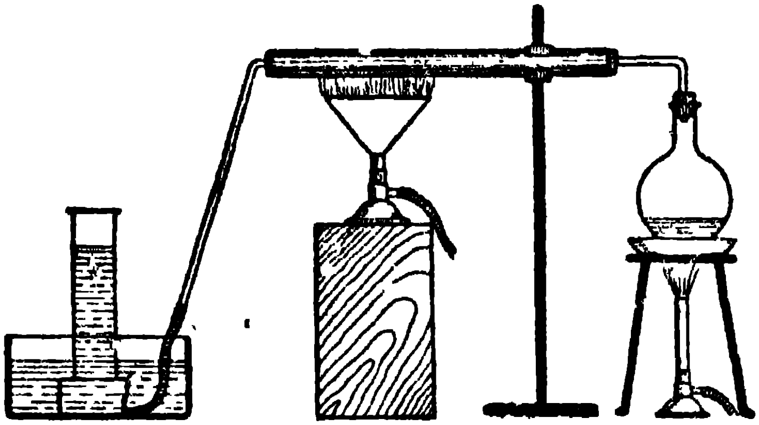

FIG. 11.

Exp. 37.—Fit up and arrange the apparatus shown in Fig. 11. It consists of an iron tube a foot or more in length and a little over half-an-inch in diameter, partly filled with iron turnings or small nails. It is fitted properly at the ends with corks, one being pierced by a glass tube bent at right angles and passing into the flask containing a little water, while through the other projects the delivery tube, cut off as shown above the surface of the water. A piece of rubber tube is slipped over it sufficiently long to deliver the gas into the jar. The iron tube is supported by a clamp and heated by a flat-flame Bunsen burner.

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* *Litmus* is a vegetable colouring matter, which is very sensitive to the action of many chemical substances. It turns red in acids, and substances which turn it red are said to have *an acid reaction*; it turns blue again in alkalies, or in substances having an *alkaline reaction*, and it is unaffected by water and many other substances which have a *neutral reaction*.

Blue litmus paper is prepared by dipping unglazed paper in a solution of litmus (prepared by boiling commercial litmus with water and filtering) and drying it. *Red litmus paper* is prepared in a similar way after first adding just sufficient acid to the litmus solution to turn it red.

Heat the iron tube as strongly as possible, and boil the water in the flask, which should rest on a sand bath. Steam passes over the red-hot nails, and a gas can be collected in the jar.* When sufficient gas has been collected, first remove the rubber portion of the delivery tube, then the Bunsen with spreading flame, and lastly, when the iron tube is no longer red-hot, the Bunsen underneath the flask.

Note.—The water in the flask must be kept boiling while the gas is being collected, or water may be forced back into the iron tube and cause a slight explosion. If it should cease to boil, at once remove the rubber portion of the delivery tube.

Test the gas in the jar with a lighted match. It burns with a practically non-luminous flame. It is *hydrogen.* Turn out the residue in the tube and examine it. The turnings or nails now resemble in appearance the blue-black substance produced when we burnt iron in oxygen (Exp. 28). They are, in fact, coated with the same substance—oxide of iron, and this compound is also formed when iron is heated strongly in air (the so-called "smithy scales" which form on the blacksmith's anvil also consist of it).

(*c*) *Magnesium.*

Exp. 38.—Put into some water a piece of magnesium ribbon, scraped so that the surface is quite bright. You will find that no gas is evolved and the metal is not tarnished.

Exp. 39.—Now repeat Exp. 37, using a coil of magnesium ribbon in place of iron turnings, and replacing the iron tube by one made of porcelain or hard glass. You will find that the same gas is evolved as in Exp. 37. Examine the residue in the tube. It is a white substance resembling that obtained by burning magnesium in air or oxygen; it is, in fact, the same substance—oxide of magnesium.

Magnesium then, like iron, reacts with water at red heat with liberation of hydrogen and formation of oxide of magnesium.

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* Before collecting any gas in the jar you must take care that all the air has been driven out of the apparatus. To test this, collect some of the gas in a test-tube, and bring it mouth downwards to a flame. An explosion shows that air is still mixed with the hydrogen. Wait a short time and test again. When the gas ignites with only a very slight "pop," you may proceed to fill the jars. *Neglect of this precaution and want of care in keeping flames away from the delivery tube have often caused serious accidents*, because air and hydrogen form an explosive mixture.

(*d*) *Copper.*

Exp. 40.—Repeat Exp. 38, using copper instead of magnesium. You will find that the copper is not tarnished.

Now repeat Exp. 37, using copper turnings and a porcelain or hard glass tube. No gas will be evolved (after the air has been driven out of the apparatus), and on examining the residue in the tube you will find that the copper has undergone no change.

Copper then is not acted upon by water, either in the cold or at a red heat.

The student might continue the experiments with other metals. He would find, for example, that potassium would behave like sodium, zinc like magnesium, tin like copper, and so on.

28. **Composition of Water.**—We have seen in Exps. 37 and 39 that iron and magnesium react with steam with liberation of hydrogen and formation of the same substances which are obtained when these metals are burnt in oxygen, *i.e.* the oxides of iron and magnesium. These results can readily be explained if we assume that *water is a compound of hydrogen and oxygen*, for the changes which have taken place can then be represented thus:—

Water (composed of **hydrogen** and **oxygen**) acted on by a **metal** yields **hydrogen** and the **oxide of the metal** (composed of the **metal** and **oxygen**).

If this is the true explanation, then we should be able to obtain water by the combination of hydrogen and oxygen.

Before attempting to do this, we will investigate a more convenient method for the preparation of hydrogen in quantity, and will study its properties more fully.

29. **Preparation of Hydrogen.**—

Exp. 41.—Introduce into a 12-oz. flask, fitted with safety funnel and delivery tube as shown in Fig. 12, 10 gms. of zinc, and add 180 c.c. of dilute sulphuric acid.* Bubbles of gas will be observed to rise at the zinc, and the gas passing out of the delivery tube may be collected in glass cylinders as shown, *taking the precautions referred to in the footnote on p. 35.* [Reserve the residue in the flask.]

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* Made by pouring sulphuric acid ("oil of vitriol") slowly with gentle agitation into eight or ten times its volume of cold water. The acid is said to be "diluted" with water.

Properties of Hydrogen.—The properties of the gas may be investigated by carrying out the following experiments—

Exp. 42. (a)—Take a cylinder of the gas, and, holding it mouth downwards, apply a light. Notice that the hydrogen burns with a pale blue practically non-luminous flame, and that the burning takes place only at the *mouth* of the cylinder, *i. e.* where it has access to air; also that a lighted taper pushed up into the cylinder whilst the hydrogen is burning will be extinguished.

(b) Hold a cylinder full of the gas mouth downwards for a short time; then apply a light and notice that very little of the gas seems to have escaped.

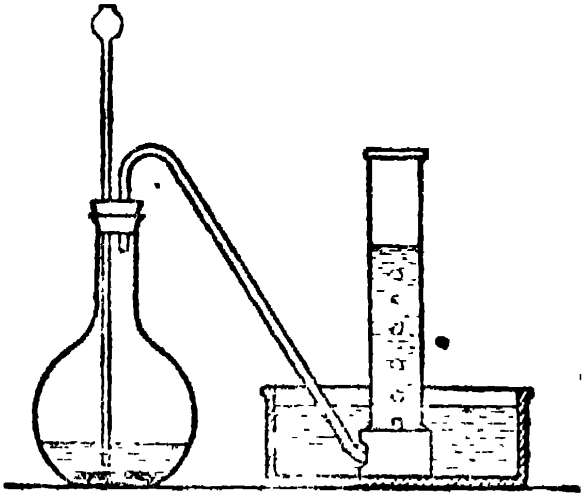

FIG. 12.

(c) Stand a cylinder on the bench mouth upwards, without cover, for a short time. Test this now with a light. You will find no hydrogen there.

(d) Take a *dry* cylinder, somewhat smaller than those used for collecting the gas, and, holding it mouth downwards, transfer the hydrogen from one of the cylinders into it by pouring upwards. The hydrogen will rise in the dry cylinder and displace the air from it. Now apply a light to the mouth of this cylinder and there will be a slight explosion, owing to a small admixture of air during the transference, whilst the gas will burn and moisture appear on the sides of the cylinder.

(e) Invert a cylinder about two-thirds full of hydrogen (the rest being water) in a trough of water. Mark the level of the liquid in the cylinder. After some time examine it again. There is no appreciable change in level, showing that if hydrogen dissolves in water at all its solubility is only very small.

b, c, d of Exp. 42 illustrate the extreme lightness of hydrogen.

30. Formation of Water by burning Hydrogen in Air.—

Exp. 43.—Take the hydrogen apparatus used above, replacing the long delivery tube by a shorter one leading to one arm of a U-tube containing calcium chloride. Attach a piece of glass tubing, bent as shown in Fig. 13, to the other arm of the U-tube. The object of this tube is to dry the hydrogen before burning it, calcium chloride being a substance which very readily absorbs moisture.* Place some granulated zinc (about 10 gms.) in the flask, and add a little dilute sulphuric acid. A gentle effervescence of hydrogen will take place, and the air will be driven out. Before we light the hydrogen we must be sure that all the air has been expelled from the apparatus by collecting some of the issuing gas in a test-tube placed over the end of the delivery tube, and testing it in the manner already described (see footnote, p. 35).

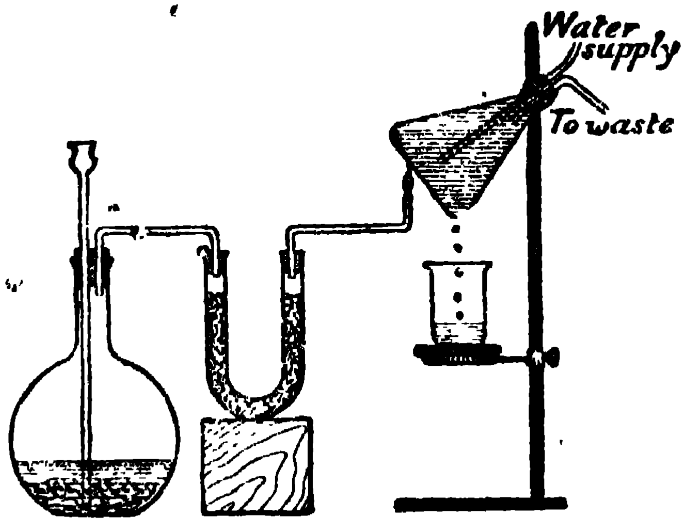

FIG. 13.

While you are waiting for the air to be driven out of the apparatus, fit up a flask with two delivery tubes, one reaching to the bottom of the flask, the other just below the cork, and support it by means of a retort-stand and clamp as shown in the diagram. Connect the delivery tube which reaches to the bottom of the flask to a tap by means of rubber tubing; also attach a piece of rubber tubing to the short delivery tube and allow the loose end of it to dip into a sink. Turn on the tap; water will flow into the flask, fill it, and then overflow into the sink. Leave the tap turned on slightly so that a slow stream of water flows through the flask.

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* It is obvious that the hydrogen must be *dry*, or the experiment does not prove that the water which collects in the beaker has been produced by the burning of the hydrogen.

When you have lighted the hydrogen jet place the flask in position over it as shown in Fig. 13; also place a beaker in the position indicated. Almost immediately moisture appears to be forming on the bottom of the flask, and soon drops of liquid trickle down and fall into the beaker. [The reason for keeping a stream of cold water running through the flask will now be obvious. It keeps the flask cool and aids the condensation of the liquid formed by the burning of the hydrogen.]

What is this liquid? It looks like water. If we examine its properties, we shall find that (1) it is colourless; (2) it has no smell; (3) it has no taste; (4) it does not burn; (5) it leaves no residue on evaporation; (6) it has no action on litmus papers; (7) its density is 1 (1 c.c. weighs 1 gm.); (8) it freezes at 0° C.; (9) it boils at 100° C.; (10) it restores the blue colour to anhydrous copper sulphate. Hence we conclude that it is *water.*

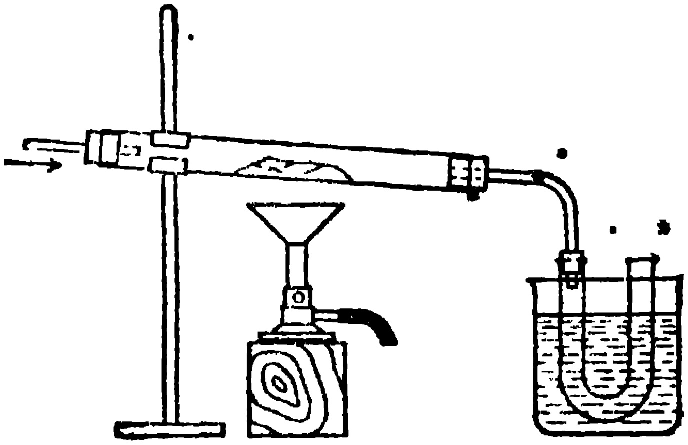

FIG. 14.

When hydrogen, then, burns in ordinary air it forms water; it was called *hydrogen* (water-former) on this account. The hydrogen must have combined with either the oxygen or the nitrogen of the air or with both. From our previous experiments (see § 28), we know that it must be with the oxygen *only.* The anticipation made in § 28 that we should be able to obtain water by the combination of hydrogen and oxygen has therefore been realised. The experiment described in the following paragraph shows how this combination may be brought about in a different way.

Formation of Water by the Action of Hydrogen on Oxides.—

Exp. 44.- Take a piece of infusible glass tubing about 30 cms. long and say 1 cm. bore, and put into it a layer of dry copper oxide. Support the tube in a slightly inclined position as shown in Fig. 14 and connect the higher end with a supply of dry hydrogen (prepared and dried as in § 67). Connect the other end with a U-tube partly immersed in a beaker of water. First the oxide is not heated and there is no apparent change; then it is heated * strongly, using a flat-flame burner, when it changes gradually into red metallic copper and a liquid collects in the U-tube which can be proved to be water by the usual tests.

The experiment may be repeated using litharge (oxide of lead) or red precipitate (oxide of mercury). In the former case beads of metallic lead collect in the tube and in the latter a mirror of mercury is produced, whilst in both water collects in the U-tube.

We see, then, that when hydrogen is passed over some heated oxides it takes up oxygen, forming water, and leaves behind the metal.

31. Oxidation and Reduction.—The *addition of oxygen* to a substance is called *oxidation.* Thus when hydrogen burns in air, when iron rusts or when lead is heated in air, oxygen is taken up and the hydrogen, iron and lead undergo oxidation. On the other hand the *removal of oxygen* from a substance is called *reduction.* The removal of oxygen from heated metallic oxides by hydrogen as in Exp. 44 is an example of reduction, the hydrogen *reducing* the oxide to the metal. But the hydrogen has taken up the oxygen of the oxide and has therefore undergone *oxidation,* i. e. the processes of reduction and oxidation have taken place *simultaneously,* and we may look upon changes such as these from two points of view: (1) as the reduction of the metallic oxide by hydrogen, and (2) as the oxidation of the hydrogen by the metallic oxide. If you refer back to Exp. 12 you will see that charcoal also is able to effect reduction or removal of oxygen, and you will understand the use of coal or coke in the smelting of iron, copper, or other metals from their ores. Hydrogen and carbon are spoken of as *reducing agents.*

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* The same precautions are necessary here as when the hydrogen was caused to burn as a jet; that is, the issuing gas must be tested to see if it is free from air before the tube is heated. The apparatus, too, should be made *air-tight.* This latter precaution is *very important.*

32. Decomposition of Water by the Electric Current—Composition of Water by Volume.—Let us now investigate an entirely different method of determining the constituents of water.

It will be instructive to examine first a peculiar phenomenon which appears when metals are placed in dilute acid.

Exp. 45.—To produce an Electric Current.—For this purpose you will require thin clean plates of copper and zinc,* say about 15 cm. long and 10 cm. wide. Dip these separately for a moment into a beaker containing dilute sulphuric acid, and note that the copper plate is unaffected, but the bubbles of gas rise from the zinc plate. Now withdraw the zinc plate, and dipping it in still weaker acid, rub the surface with a little mercury until it shows a bright lustre. The upper part of the plate which stood above the level of the acid in the beaker need not be covered with mercury. Now again dip both the plates in the beaker containing acid; nothing happens at either plate. Bring the upper edges of the two plates together; bubbles of gas rise from the *copper* plate. Separate the plates and bring them together again several times; the action ceases on separation but commences again immediately the plates touch.

Now connect copper wires by binding screws to the upper edges of the two plates.

Observe (1) that when you keep the wires apart there is no evidence of action going on in the beaker, but that when you bring the ends of the wires together the action is set up just as it was when the edges of the plates were brought together, and that now a small spark appears when the wires touch. (2) That if you bring a small compass-needle just below the wire, and then bring the ends into contact, the needle will be turned aside each time you make contact.

If you try to do either of these things simply with two pieces of copper wire, you will then be convinced that there is something present in the wires owing to their attachment to the metal plates in the acid. Metal plates so arranged are called a *voltaic cell.* By fitting up several of them, and joining the zinc in one cell to the copper in the next by copper wire, and finally attaching two lengths of copper wire, one to the copper in the first cell, and the other to the zinc in the last cell, you may fit up a *voltaic battery*, and produce stronger effects than you can do with one cell.

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* Plates of other metals may be also tried in the same way.

There is a *third* effect that may be shown to accompany the passage of the electric current along the wires.

Exp. 46.—Procure two pieces of platinum foil about 5 cms. long and 2 cms. broad. Prick a row of holes down the middle of each and thread the terminal ends of the wires through them. Take now a small beaker of distilled water and dip into it the two platinum plates (they are called *electrodes*); nothing happens. Add a few drops of dilute sulphuric acid to the water; bubbles of gas rise freely from both electrodes.

The current of electricity is unable to pass through pure water and make itself felt, but it can pass through acidulated water. By a suitable arrangement the gases evolved may be collected and examined.

Exp. 47.—Take a large bell jar and paste a thin strip of paper round the side of it about half-way up, arranging so that the two ends meet and form a circle round the jar. With a sharp file scratch a line just above the strip of paper (which enables you to keep the line straight). When the scratch forms a complete circle take a glass rod, heat the end red-hot in a Bunsen flame, and touch the scratch with it. The jar will break into two halves. Take the upper half and rub the rough edge with coarse emery paper till it is smooth.

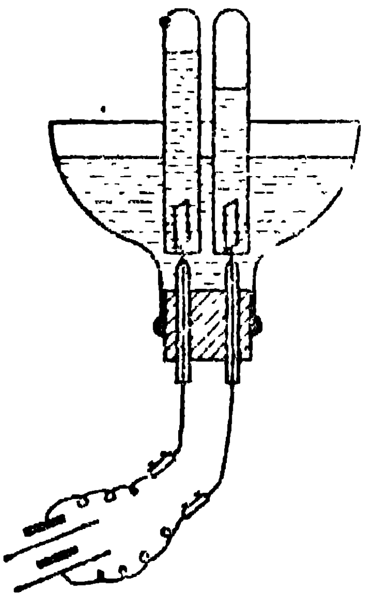

FIG. 15.

Now take two pieces of platinum wire about 6 inches long and attach them to two pieces of platinum foil of the size mentioned in Exp. 46 (in the way described there). Fuse the wires into pieces of narrow glass tubing about 3 inches long, as shown in Fig. 15. Procure a two-holed rubber cork which fits the jar, push the glass tubes into it, and insert the cork (see diagram).

Now pour water, to which a little dilute sulphuric acid has been added, into the jar till the electrodes are covered; also fill two test-tubes with the same liquid and invert them over the electrodes. Connect the wires by binding screws with the leads from a battery of 3 or 4 Grove's cells. As soon as the connection is made gas is seen to rise from the electrodes and collect in the tubes. Further, the volume of gas collecting over the electrode connected with the zinc plate of the battery (called the *negative pole*) will be found to be twice that collecting over the electrode connected with the platinum plate (which corresponds to the copper plate of our simple cell and is called the *positive pole*). Examine the gases with a lighted splint of wood; you will find that the gas collected in larger quantity is *hydrogen*, that in smaller quantity *oxygen*.

Subject to the possibility that it is something in the sulphuric acid with which we are at present insufficiently acquainted that gives us the hydrogen and oxygen, we should conclude that water yields by its decomposition hydrogen and oxygen, and further that it is composed of these two elements *in the proportion of two to one by volume*. That this is the case may be conclusively proved by the following experiment*—

Exp. 48.—A long graduated glass tube (called a *eudiometer*), having two platinum wires passed into it near one end, which is closed (Fig. 16), is taken and filled with mercury and inverted in mercury. Some hydrogen is passed in, and then exactly half the volume of oxygen.† On connecting the platinum wires with a battery and induction coil and passing an electric spark through the mixture there is an explosion. After a time we find the mercury fills the entire tube. This proves that the gases have completely combined and that they were present in the proper proportions to form water. Cavendish was the first to establish this fact (1781).

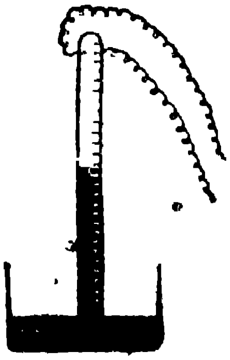

FIG. 16.

We have now determined the quantitative composition of water in two ways: in Exp. 47 by *decomposing* it into its constituent elements, *i.e.* by *analysis*, in Exp. 48 by *combining* the constituent elements, *i.e.* by *synthesis*.

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* The student is not advised to perform this experiment.

† The most convenient way is to use the mixture of hydrogen and oxygen produced by the electrolysis of water. The gases are then present in the correct proportion.

QUESTIONS.—CHAPTER IV.

1. What happens when dilute sulphuric acid is poured upon zinc? How would you collect the gas given off? Sketch the apparatus you would use. Describe experiments to show that it is a very light substance.
2. How would you prove conclusively that when hydrogen burns in air water is formed?
3. Describe all that you may see when a piece of sodium is thrown on water in a dish. How does the water differ, after the sodium has disappeared, from pure water?
4. What metals are known to you capable of decomposing water? How do they act respectively? Sketch the apparatus that would be required to collect the hydrogen evolved by the use of any one of these metals.
5. How has the composition of water by volume been established analytically and synthetically?
6. Describe how you would proceed to prepare water from a metallic oxide by the action of hydrogen. Sketch the necessary apparatus.
7. What do you understand by the terms *oxidation* and *reduction*. Give examples of these processes.

CHAPTER V.

ACIDS, SALTS, BASES.

33. Properties of Acids.—

(*a*) *Sourness.*

Exp. 49 (a).—Introduce *one drop* of dilute* hydrochloric acid (*spirit of salt*) and one drop of dilute sulphuric acid respectively into clean test-tubes and nearly fill the tubes with water. Shake up and then taste the liquids. They are sour.

Vinegar also is sour. *Sourness* is a characteristic property of a large class of bodies called *acids.*

(*b*) *Action on Litmus.*

Exp. 49 (b).—Pour a little dilute hydrochloric acid and a little dilute sulphuric acid into separate beakers and dip pieces of blue litmus paper into them. The colour changes to *bright red.*

(*c*) *Action on Metals.*

Exp. 49 (c).—Fill a test-tube about one-third full of dilute sulphuric acid and introduce some small pieces of magnesium ribbon. Notice that there is a violent effervescence of gas and that the tube soon becomes warm. After a short time apply a light to the mouth of the tube. The gas ignites with a slight explosion and burns with an almost non-luminous flame. It is *hydrogen.*

You may find that when most of the magnesium has dissolved colourless crystals separate out in the tube. If they do not, filter the liquid, evaporate to small bulk in a porcelain dish, and allow to cool Colourless crystals separate out. These consist of a substance called *magnesium sulphate.* Magnesium has taken the place of the hydrogen of the acid. Instead of *sulphuric acid* and *magnesium,* we have now *hydrogen* and *magnesium sulphate.*

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* "Dilute" hydrochloric acid is obtained by adding two or three volumes of water to one volume of the strong acid.

Exp. 49 (d).—We have already found in Exp. 41 that hydrogen is evolved by the action of dilute sulphuric acid on the metal zinc. Examine the residue in the flask (which you have reserved). You will observe that colourless crystals have separated out. These consist of *white vitriol* or *zinc sulphate*. The zinc has replaced the hydrogen of the acid, with formation of zinc sulphate.

In order to obtain the zinc sulphate free from metallic particles, pour a little water into the flask and warm till the crystals dissolve. Now filter, evaporate the filtrate slightly, and cool. Crystals separate out.

Similar results are obtained if iron is treated with dilute sulphuric acid; also if hydrochloric acid or acetic acid is used with any of these metals instead of sulphuric acid. Here, then, we have a third characteristic of an acid, namely, that it acts upon certain metals, such as iron, zinc, and magnesium, with liberation of hydrogen and formation of crystalline substances.

34. **Salts.**—The crystalline substances produced by the action of metals on acids are termed *salts*. Let us see whether or not they behave like acids towards litmus.

Exp. 50.—Filter off the crystals of magnesium sulphate obtained in Exp. 49 (*c*). Wash them carefully* with a little water, and then dissolve in water. Test the solution with (1) blue litmus paper, (2) red litmus paper. You will find that neither is affected; *i. e.* magnesium sulphate is *neutral* to litmus.

Repeat the experiment with the crystals of white vitriol obtained in Exp. 49 (*d*). You will find that white vitriol is also neutral to litmus.

The replacement of hydrogen in sulphuric acid by magnesium or zinc has removed from the acid one of its characteristic properties—that of turning blue litmus red. The salts derived from other acids are also neutral to litmus in the majority of cases. Since, then, an acid is no longer an acid after its hydrogen has been removed, it follows that *hydrogen is an essential constituent of acids.*

The salts derived from sulphuric acid are called *sulphates;* those from hydrochloric acid *chlorides;* those from nitric acid *nitrates;* and so on.

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* The success of this experiment depends upon the care with which the crystals are washed. Unless the adhering acid is completely removed the solution of the salt will of course be acid to litmus.

35. Formation of Acids from Non-metals.—

Exp. 51.—Burn some sulphur in air as in Exp. 24. Remove the deflagrating spoon, pour a little water into the jar, drop in a piece of blue litmus paper and at once cover with a greased glass plate. Shake up. Notice that the white fumes disappear and the blue litmus is reddened, showing that an acid has been formed. Invert the jar in a trough of water and remove the glass plate; the water rises in the jar.

Pour a little of the acid liquid in the jar into a porcelain basin and boil it. Notice that after a time the smell disappears. Now test the remaining liquid with blue litmus paper; the litmus is not affected.

The results obtained in the previous experiment are in accordance with the following explanation:—The sulphur in burning combines with oxygen to form an oxide of sulphur—*sulphur dioxide*. This substance is a gas which dissolves very readily in water, with which it combines forming an acid—sulphurous acid. [That sulphur dioxide *alone* is not an acid is proved by the fact that when quite dry it does not affect dry litmus paper; it is only when the gas is dissolved in water that it acquires acid properties: therefore in all probability the solution contains a compound of sulphur dioxide and water, though such a compound has never been isolated.] The water rises in the jar to take the place of the oxygen which has been removed.

The effect of boiling the acid solution is to decompose the acid present and drive off the sulphur dioxide in the form of gas.

You might similarly repeat Exp. 19, and show by means of litmus solution that the water in the trough becomes acid. Here the white powder formed by the combination of phosphorus with the oxygen of the air (phosphorus pentoxide) dissolves in the water, and unites with it to form an acid—phosphoric acid. This is a general property of non-metals, *i. e.* they combine with oxygen to form oxides, which unite with water with formation of acids. Such oxides are called *acidic oxides.*

36. Alkalies: Caustic Soda, Sodium Hydroxide.—We have already learnt (Exp. 36) to recognise this class of substances by the use of litmus solution. They possess the property of restoring the colour to litmus which has been reddened by the addition of acid. But they have another important property which we shall now examine.

One of the most important substances belonging to this class of bodies is that known as *caustic soda.*

Caustic soda is a substance of considerable interest and importance, and is manufactured in large quantities for various purposes, but especially for soap-making. We met with it when describing the behaviour of sodium towards water.

Exp. 52.—Examine a piece of caustic soda and observe that—

(*a*) It is a white solid, but does not seem to be crystalline.

(*b*) If left exposed to the air, it becomes moist, that is, it *deliquesces.* It would, if left long enough, run down to a liquid. It absorbs moisture from the air. Such bodies are termed *hygroscopic* or *deliquescent.*

(*c*) It dissolves very readily, as do most deliquescent bodies, in water, and considerable heat is developed during solution. The liquid thus formed has a soapy feeling.

(*d*) This solution turns reddened litmus blue.

Carefully add to this blue solution a solution of hydrochloric acid until the colour *just* becomes red. (The hydrochloric acid is conveniently run in from a long tube with a stop-cock at the bottom called a *burette.*) We have now, as it were, balanced the alkali with acid. The slightest quantity of caustic soda solution will change the colour to blue again. We have here practically a *neutral* solution. *How does it differ from the acid and the alkali?*

Boil it down to dryness. Notice that the solid produced is not like caustic soda. Taste it You will recognise it as *common salt.*

The salt has been produced by the replacement of the hydrogen of the acid by the metal sodium, *i.e.* it is the sodium salt of hydrochloric acid, or *sodium chloride.* Here, then, we have a second method of preparing salts, namely, by the action of an alkali on an acid.

An *alkali* is a *substance which possesses the property of restoring the blue colour to reddened litmus, and of neutralising acids with formation of salts.*

Caustic Potash, Potassium Hydroxide, may be examined in the same way as was caustic soda. It is an exactly similar body, and could not be distinguished from it by ordinary means. It, too, will neutralise acids, and when hydrochloric acid is used a salt termed *potassium chloride* is formed, which resembles common salt very closely, but may be distinguished from it by its taste.

37. Action of Water on Oxides of the Metals.—

Exp. 53.—Introduce a piece of sodium about the size of a pea into a deflagrating spoon, heat in a Bunsen flame until the metal ignites and then lower into a jar. The metal continues to burn, forming a dirty-white solid—oxide of sodium.* Pour in some water; the substance dissolves. Test with red litmus paper; the colour changes to blue, *i. e.* the solution is *alkaline.*

Here we have an oxide of a metal dissolving in water to form an alkali—the substance in solution is in fact caustic soda, and is formed by the combination of the oxide of sodium with water.

Exp. 54.—Moisten several pieces of red litmus paper and place on them small quantities of the following metallic oxides (finely powdered): quicklime, litharge, magnesia, red precipitate, black oxide of copper, red oxide of iron (rouge). You will find that quicklime turns the litmus bright blue, litharge, magnesia, and red precipitate turn it slightly blue, whilst the oxides of copper and iron do not affect it.

Now shake up some of each of these oxides with water, filter and evaporate the filtrates to dryness. You will find that only in the case of lime is there any appreciable residue, *i. e.* only lime is soluble in water to any great extent. The other oxides which change the colour of the litmus can, however, be shown to be slightly soluble in water.

Oxides of metals, then, if they dissolve in water at all, give rise to alkalies, if not they behave as neutral bodies.

38. Action of Metallic Oxides on Acids—Bases.—

Exp. 55.—Add finely-powdered black oxide of copper gradually to a little dilute sulphuric acid, shaking up after each addition. The oxide dissolves at first, forming a blue solution, and if you test the liquid from time to time with blue litmus paper you will find that the red colour formed becomes gradually less vivid, showing that the acid is being gradually neutralised. After a time no more oxide dissolves, and if the liquid is filtered and the filtrate allowed to stand, blue crystals separate out.

The crystals obtained in Exp. 55 consist of copper sulphate, a salt derived from sulphuric acid by the replacement of the hydrogen by the copper of the copper oxide.

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* Or more correctly a mixture of two oxides.

At the same time the hydrogen of the acid and the oxygen of the copper oxide unite to form water.

Most metallic oxides will be found to behave in a similar way towards acids. Further, if the salts formed are strongly heated in air they very frequently undergo decomposition; acid fumes are produced, and a residue of metallic oxide remains. It was on this account that metallic oxides were called "bases" by the early chemists, the oxide being the *base of the salt*, i. e. the residue remaining when the salt was strongly heated. The term is still applied to metallic oxides, which are also called *basic oxides;* it is also applied to compounds of metals with hydrogen and oxygen, *i. e.* to metallic *hydroxides* (caustic soda and caustic potash are examples). The terms acid, base and salt are concisely connected together in the following statement:—

Acid + Base yield Salt + Water.

A few bases which dissolve in water, forming solutions which turn red litmus blue (*e. g.* caustic soda), are called *alkalies*, so that an alkali is a particularly active kind of base.

39. **Metals and Non-Metals.**—There is little difficulty in recognising the commoner metals by means of their physical properties; they are generally heavy, solid, and opaque, good conductors of heat and electricity, and when freshly scratched or cut exhibit a characteristic lustre. Similarly the common non-metals (*i. e.* the elements which are *not metals*) are easily recognised because their properties are in general the opposite of those just mentioned. Thus iron and silver are unmistakably metals, and phosphorus and oxygen non-metals. But in the case of some elements it is very difficult to say whether they are metals or non-metals; as one element may at the same time exhibit properties belonging to both classes.

From the chemist's point of view, however, an examination of the chemical properties of an element provides a more definite distinction than that of its physical properties. We have seen above that some elements form basic oxides, whilst others give rise to acidic oxides, and that the former property is characteristic of the metals and the latter of the non-metals. This distinguishing chemical property along with others is considered in the following list:—

Characteristic Chemical Properties of Metals.—

(1) Metals form basic oxides.

(2) Metals usually dissolve in dilute mineral * acids with evolution of hydrogen.

(3) Metals either do not combine with hydrogen or form unstable compounds with it.

Characteristic Chemical Properties of Non-Metals.—

(1) Non-Metals form acidic oxides.

(2) Non-Metals are not acted upon by dilute mineral acids.

(3) Non-metals usually form stable compounds with hydrogen.

The metals are also distinguished by the fact that when exposed to air or oxygen, especially when heated, they usually lose their brightness of surface and become dull; the non-metals either undergo no change at all, or are acted upon much less readily.

We have already mentioned that the two classes exhibit distinct *physical* properties, by which they are popularly distinguished.

Characteristic Physical Properties of Metals.—

(1) They are solids at ordinary temperatures (except mercury).

(2) They reflect light well, especially at a polished or freshly-cut surface; in short, they possess a pronounced lustre.

(3) They are often capable of being hammered into plates or drawn into wire; in other words, they are malleable and ductile.

(4) They have usually a high specific gravity.

(5) They are good conductors of heat and electricity.

(6) They are volatilised, as a rule, only at very high temperatures.

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* *Mineral* acids are acids which are derived from mineral matter, such as hydrochloric and sulphuric acids.

Characteristic Physical Properties of Non-Metals.—

(1) They may be gases, liquids or solids at ordinary temperatures.

(2) They do not, as a rule, reflect light well.

(3) They are brittle if solid.

(4) They generally have a low specific gravity.

(5) They are usually bad conductors of heat and electricity.

(6) Those which are not gases at ordinary temperatures, are transformed into the gaseous condition at comparatively low temperatures, except in three notable cases, viz. carbon, silicon and boron.

Each of these properties may be exceptionally absent, and must be accepted as only indicating generally the characters of metals when compared with non-metals. It cannot be said that they furnish a means of drawing a sharp line of demarcation between the two classes. Gold and platinum may be precipitated as black powders, though they regain their lustre on being burnished by rubbing with a piece of smooth agate or steel. The non-metals, silicon, boron, iodine, and carbon in the form of diamond and graphite, possess lustre, which differs, however, from the peculiar lustre which can only be described as "metallic." Again, some metals have quite low specific gravities; lithium, sodium and potassium, for instance, are lighter than water, and the specific gravities of magnesium and aluminium are only 1·75 and 2·6 respectively, whereas that of platinum is 21·5; on the other hand, diamond has a specific gravity 3·5, *i. e.* it is twice as heavy as magnesium. Carbon, in the form of graphite, is a good conductor of both heat and electricity. The three elements carbon, silicon, and boron are conspicuous from the fact that they are more difficult to volatilise than any of the metals.

There are a few elements which cannot satisfactorily be placed in either class. Thus arsenic and antimony, in their physical properties, resemble the metals, since they have a metallic lustre and are good conductors of heat and electricity; in their chemical properties, however, they resemble the non-metals; for they form acidic oxides and are insoluble in dilute mineral acids. Such elements are called *metalloids.*

Hydrogen, again, is another element which is difficult to classify. Its physical properties (except the fact that it conducts heat) and some of its chemical properties place it amongst the non-metals; but, since metals will displace hydrogen from acids and will also displace other metals from their salts, hydrogen might be considered to be a metal. It is best to put it with the metalloids.

In the list of elements at the end of Chapter VIII. the non-metals are indicated by italic type.

QUESTIONS.—CHAPTER V.

1. What is a *salt?* How would you prepare the following :—(1) potassium chloride from caustic potash; (2) copper sulphate from black oxide of copper?
2. What are the distinguishing characters of *acids?* Describe the experiments you would perform in order to illustrate them.
3. Describe the properties of any common alkali known to you. Mention also two other examples of alkalies.
4. Describe how you would proceed to investigate the action of water on the following oxides :—sulphur dioxide, quicklime, oxide of phosphorus, black oxide of copper, litharge. State the results you would obtain. Into what classes would you be led to divide oxides as a result of your investigations?
5. Into what two classes may elements be divided? What are the characteristic properties of each class?
6. What are *metalloids?* Illustrate your answer by discussing examples.
7. State fully how you would proceed to investigate whether a given solid substance was a metal or a non-metal.

8. Describe some experiments to illustrate the chief properties of some *common alkali* known to you.
9. A solution of caustic soda is gradually added to a little hydrochloric acid to which a little litmus solution has been added. State and explain the colour-changes which take place.
10. Explain why the early chemists called the oxides of the metals *bases*.

Describe an experiment to illustrate the action of an acid on a base.

CHAPTER VI.

CARBON DIOXIDE.

40. Action of Heat on Chalk.—

Exp. 56.—Place a little powdered chalk in a porcelain crucible and weigh the whole. Hold in the crucible a glass rod with a drop of lime-water on the end; the lime-water remains clear. Heat the powder to bright redness for a few minutes and then test again with lime-water; it becomes milky, showing that a gas is present in the tube which was not there before. Continue the heating for a few minutes longer, allow the crucible to cool in the desiccator and reweigh. You will find that there is a loss in weight. Test the white residue with damp red litmus paper; the colour changes to blue, *i. e.* the residue has an alkaline reaction. Similarly test the chalk and note that it does not affect litmus.

We may conclude from this experiment that when chalk is heated it breaks up into a colourless gas which turns lime-water milky, and a white solid which behaves as an alkali. The loss of weight is due to the removal of the gas, which is called *carbon dioxide*, the alkali is *quicklime*. Chalk is therefore a compound of quicklime and carbon dioxide. Limestone, marble, and shells break up in a similar manner on heating; hence they are composed of the same two substances.

41. Preparation of Carbon Dioxide.—The method we have adopted in Exp. 56 is not the readiest means of preparing carbon dioxide from chalk or limestone. The gas is evolved much more easily by the action of a dilute acid—preferably hydrochloric acid.

Exp. 57.—Put some lumps of limestone or chalk into a flask of suitable capacity—say half a litre. Fit with a thistle funnel reaching nearly to the bottom, and a delivery tube bent twice at right angles. Connect this with a Woulff's bottle containing a little water so that the tube dips well into the liquid. The water will dissolve any hydrochloric acid (which is itself a very soluble gas) that may accompany the dioxide (see Fig. 17). Convey the "washed" gas to the bottom of the collecting jars, etc.; while filling cover their mouths with cardboard. Pour in sufficient water to cover the limestone; then add through the funnel some dilute hydrochloric acid. Collect three jars of the gas and allow the rest to bubble through a little distilled water.

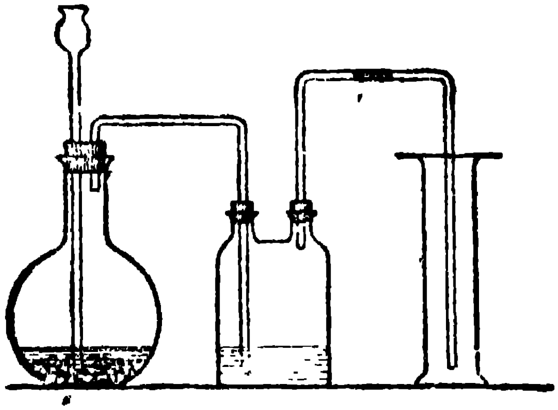

Fig. 17.

To see when each jar is full, hold a lighted match near its mouth, when the heavy overflowing gas will extinguish the flame.

Properties of Carbon Dioxide.—

Exp. 58 (a).—First show that the colourless gas you have collected is carbon dioxide by adding a little lime-water to one of the jars and shaking up. The characteristic milkiness will appear.

(b).—To demonstrate its heavy nature.—Set a wide bell-jar in an inverted position. Sprinkle a small handful of powdered chalk or "whiting" in the bottom and pour upon it some dilute hydrochloric acid. A considerable amount of the gas is quickly evolved, and an ordinary soap-bubble dropped into the jar will float where the gas and air meet.

(c).—Its effect upon burning bodies.—Pour a jar of the gas into another and wider jar in the bottom of which a bit of candle is burning. The flame is extinguished. The experiment further illustrates the high density of the gas.

It has been found that air, 2·5 per cent. only of whose oxygen has been converted into carbon dioxide, will not allow ordinary bodies to burn in it. On this account various vessels containing carbon dioxide under pressure have been designed for the extinction of fires.

Exp. 58 (d).—Its solubility in water.—Divide the water through which the gas bubbled into two parts.

1st part.—Taste this; then test it with a blue litmus paper. The reddening shows the presence of acid although the liquid is not distinctly sour. The gas itself was formerly called "carbonic acid"; but the dry gas does not affect a dry blue litmus paper, hence the term is a misnomer. Heat the liquid until it boils, and continue the boiling for a few minutes. Observe that during the heating gas bubbles rise through the liquid and escape. Now test again with blue litmus paper. The colour is not affected. Evidently carbon dioxide is soluble in cold water, and apparently the gas and the water unite to form an acid, but this acid is very unstable, and breaks up again into carbon dioxide and water on heating; the carbon dioxide escapes, being insoluble in boiling water.

2nd part.—Add a little lime-water. The liquid becomes milky, proving the presence of carbon dioxide.

Now test the liquid you have boiled (1st part) with lime-water. No precipitate should appear, confirming the fact that boiling has expelled the gas.

42. Carbon Dioxide formed when Charcoal, Wood, etc., burn.—

Exp. 59.—Burn some charcoal in oxygen as described in Exp. 26. Pour a little lime-water into the jar and shake up. The lime-water becomes milky, showing that the carbon dioxide has been formed. Also burn charcoal in air as described in Exp. 10. Prove that carbon dioxide is being evolved by holding a glass rod with a drop of lime-water on the end in the mouth of the crucible.

It is clear, then, that charcoal when it burns combines with oxygen to form carbon dioxide, *i. e.* carbon dioxide is (as its name implies) a compound of carbon and oxygen (charcoal is a form of carbon). Carbon dioxide is also formed when substances such as wood, coal, paraffin, etc., which contain carbon in large quantities, are burnt.

Exp. 60.—Fasten a match on to a piece of wire, ignite it and lower it into a small gas-jar. When the flame goes out prove the presence of carbon dioxide in the jar by means of lime-water. Similar experiments may be performed with a piece of candle, etc.

We have proved in Exp. 59 that carbon dioxide is a compound of carbon and oxygen. This being the case it should be possible to recover the carbon from the gas if we can find a substance which has a stronger attraction for oxygen than carbon. Such a substance is metallic magnesium.

Exp. 61.—To extract the carbon from carbon dioxide.—Ignite a strip of magnesium ribbon tied to a deflagrating spoon, and plunge it into the gas. The metal continues to burn, and, on examination of the solid formed, white magnesium oxide will be found together with black specks of carbon.

On the other hand most metals have less attraction for oxygen than carbon. We have had an example of this in Exp. 12, where carbon removed oxygen from litharge, forming carbon dioxide and leaving metallic lead.

43. Formation of Carbon Dioxide by Living Organisms.—

Animals.—The food material of animals—such as meat, vegetable tissue, sugar, etc.—contains a considerable quantity of carbon. As the food undergoes decomposition in an animal's body, much of the carbon unites with oxygen in its blood derived from the air through the medium of its lungs. Carbon dioxide is thus formed, and is returned to the air through the same medium. Its presence may be readily detected in expired breath by blowing through a tube dipping into some lime-water. The lime-water soon becomes milky. [Try the experiment.]

Plants.—(1) *Respiration* in plants is a similar, but slower, oxidation process. The stored starch is broken up, and carbon dioxide is expelled into the air as a result. This process is not confined to the green parts of plants, and it goes on by night as well as day; but it is only under certain special conditions that this can be detected easily. Germinating seeds, however, show it well.

Exp. 62 (a).—Suspend a thermometer with its bulb in some wheat, oats, or peas, etc., placed in a funnel and kept damp. They presently germinate or "sprout," and will be found to be of a higher temperature than the surrounding air.

The rise in temperature is evidence that chemical change is taking place.

Exp. 62 (b).—Place a small vessel containing lime-water amongst some of the germinating seeds when transferred to a beaker. Cover the beaker with a glass plate. The lime-water speedily becomes milky.

This experiment proves that during the chemical change carbon dioxide is formed.

(2) In *fermentation* such as occurs in breweries, minute unicellular plants which form the yeast contain in their cells a substance which decomposes dissolved sugar. The break up of the sugar gives rise to large quantities of carbon dioxide as well as alcohol.

Exp. 62 (c).—Half fill a large flask with water moderately sweetened with common brown sugar. Add some brewer's yeast; then fit the flask with a cork and a delivery tube leading into some lime-water, and stand it in a warm place. Carbon dioxide will be slowly expelled and give its characteristic reaction.

QUESTIONS.—CHAPTER VI.

1. Describe how you would prepare and collect a few jars of carbon dioxide. Sketch the apparatus you would use, and explain the use of each part. What experiments would you perform in order to illustrate the chief properties of the gas?
2. In what different ways can carbon dioxide be obtained?
3. Describe how you would proceed to investigate the action of heat on chalk.
4. Describe an experiment by which you could obtain free carbon from carbon dioxide.

CHAPTER VII.

CONSERVATION OF MATTER—LAWS OF DEFINITE AND MULTIPLE PROPORTIONS.

44. The Conservation of Matter.—With the aid of the chemical balance we are now in a position to approach a question of very great importance which as yet has not been touched upon. During the changes which are continually being observed by chemists, is there any reason to suppose that matter may be actually destroyed or created? Let us investigate the problem by experiment.

Exp. 63 (a).—Take a clean, dry litre flask, and fit it with a good cork. Cut off from a stick of ordinary phosphorus a piece of about the size of a pea, taking care to perform this operation under water. Dry the piece of phosphorus with filter paper, place it in the flask, fit in the cork, and weigh the whole. Now ignite the phosphorus by dipping the flask into hot water. The flask will soon be filled with white fumes of oxide of phosphorus. When the flask is cool, wipe it dry and weigh again. The weight will be found to be the same as before.

(b) Take two small beakers. Pour into one a little copper sulphate solution and into the other a little caustic potash solution. Weigh the two beakers together. Now pour the caustic potash into the copper sulphate, taking care not to lose any liquid. A bulky precipitate forms. Evidently chemical change has taken place. Weigh the two beakers again together. The weight is the same as before.

It is clear that in these two experiments there has been no creation or destruction of matter but merely a redistribution. A vast number of experiments conducted on similar lines have led chemists to the conclusion that *in the course of chemical operations matter is neither destroyed nor created.* This statement is called the *Principle of Conservation of Matter*: and is one of the fundamental principles of the science of chemistry.

45. Mixtures and Compounds.—We may bring together sand and sugar, or common salt and soot, etc., *in any proportions we please*, and the first mixture will be the sweeter, and will dissolve in water the more freely the greater the proportion of the sugar is; the latter, with a predominance of soot, will be very dark in colour, and with a predominance of salt may be only faintly grey. An infinitely large number of mixtures could be made, all slightly differing in taste and appearance, and also in respect of the extent to which the mixture will dissolve in water. In any of the mixtures you might, however, by very simple means recognise the sand and the sugar, or the soot and the salt, and it is also an easy matter to separate them, *e. g.* by shaking up with water and filtering, when the sugar or salt dissolves and passes through the filter, whilst the sand or soot remains on the filter (compare Exp. 35).

Exp. 64.—Mix together intimately seven parts by weight of finely-powdered iron and four parts of flowers of sulphur. Heat one-half of the mixture over a Bunsen burner in a small porcelain crucible for a few minutes with the lid on. Allow to cool, and powder some of the product very finely. Compare with the rest of the mixture: you will notice a difference in colour. Draw a magnet through each of the powders. You will find that iron is extracted from the mixture which has not been heated, and a residue of sulphur remains. No iron can, however, be extracted from the substance formed on heating by means of a magnet; a *chemical compound* has been formed. Shake up a little of each of the powders with carbon sulphide. Filter. Allow the filtrate to evaporate. In the case of the mixture a residue of sulphur remains, but there is no residue * in the case of the compound.

Drop a little of each of the powders into some dilute sulphuric acid contained in separate test-tubes. Note that in the case of the mixture hydrogen is evolved and a residue of sulphur remains, whilst in the case of the compound an evil-smelling gas (sulphuretted hydrogen) is evolved, and no residue * remains.

In the mixture of iron and sulphur, then, the two elements retain their individual properties, iron its magnetic properties and its solubility in dilute acid with evolution of hydrogen, sulphur its solubility in carbon bisulphide, and insolubility in acid; in the compounds, on the other hand, these individual properties of the two elements are completely lost. The constituents of the mixture can readily be separated by making use of their individual properties, but the constituents of the compound cannot be separated in this way.

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* There may be a slight residue of sulphur owing to the incomplete combination of the iron and sulphur.

Similar experiments with other substances lead to similar results, and we may define a *chemical compound* as *a substance produced by the union of two or more simpler substances in such a way that the individual properties of the constituents have disappeared.* We shall in the next paragraph investigate a very important property of chemical compounds.

46. Law of Constant Proportion.—

Exp. 65 (a).—Composition of Oxide of Magnesium.—Weigh a clean, dry porcelain crucible with its lid. Measure off 12 cms. of *bright* magnesium ribbon (scrape the ribbon with a knife if it is not bright), roll it up *loosely* and place in the crucible; then weigh the whole. Fix securely on a pipeclay triangle and tripod. Heat the closed crucible sufficiently to cause the metal to burn when the lid is slightly raised. Do not let any white fumes escape. When the burning has nearly ceased remove the lid, but continue to heat for a few minutes longer. Cool and weigh the whole again. Now reheat for a short time, cool, and reweigh. If the weight has changed, you must repeat the heating, cooling, and weighing till two consecutive weighings are the same, showing that the change is complete.

Tabulate your results like this:—

	grammes.
Weight of crucible, lid, and magnesium	=
,, crucible and lid	=
,, magnesium...	=
,, crucible, lid, and magnesium oxide (1) ...	=
,, ,, ,, ,, ,, (2) and (3) (constant—suppose)	=
,, magnesium oxide	=
Increase in weight of metal, *i.e.* weight of oxygen	=

Weight of oxygen combined with one part by weight of magnesium, *i. e.*

$$\frac{\text{Weight of oxygen}}{\text{Weight of magnesium}} =$$

Now repeat the whole experiment, using a different weight of magnesium.

You will find that, however many times you perform the experiment, you will always obtain the same result on calculating out the weight of oxygen which combines with one part by weight of magnesium.

Let us now prepare oxide of magnesium from magnesium in another way and see whether the proportions of oxygen and magnesium are the same as before.

Exp. 65 (b).—Roll up a piece of magnesium ribbon about the same length as you used in the previous experiment. Place it in a beaker containing some dilute sulphuric acid, and immediately cover the beaker with a watch glass so that none of the liquid is lost by spirting. When the metal is all dissolved, wash the watch glass with a little distilled water, and allow the washings to run into the beaker; any of the liquid which spirted on to the watch glass is thus returned to the beaker. Now add excess of sodium carbonate solution, and boil; a white precipitate (magnesium carbonate) will be formed. Allow this to settle, and pour off the supernatant liquid through a filter.* Wash the precipitate several times with *small quantities* of hot distilled water, allowing the precipitate to settle each time, and then pouring off the liquid through the filter. (This is called *washing by decantation.*) Finally, transfer the precipitate to the filter, and again wash it with hot water till a drop of the liquid passing through leaves no residue when evaporated to dryness on a watch glass. This shows that all soluble salts have been washed out of the precipitate. Now place the filter in a steam oven to dry.

When the precipitate is quite dry, transfer as much of it as possible to a weighed porcelain crucible which is standing on a piece of smooth black paper. Fold the filter paper up (keeping it over the black paper meanwhile) and place it on the lid of the crucible, which you have previously placed upside down on a pipeclay triangle supported by a tripod stand. (The lid should have been weighed with the crucible.) Heat the lid by means of a Bunsen burner till the filter paper is completely burned. Transfer the ash to the crucible, and then sweep any particles of precipitate which may have fallen on to the black paper into the crucible.

Now heat the crucible to bright redness for fifteen minutes. Use a gas blowpipe and foot-blower, and take care to direct the flame upon the *bottom* of the crucible (The *gas blowpipe* consists of two tubes, one within the other. Through the inner tube air is urged, whilst gas is admitted to the annular space. Light the gas before starting the current of air.) During the last five minutes heat the crucible lid separately by means of a Bunsen burner. Cool and weigh the crucible and lid together. Reheat the crucible (keeping the lid in the desiccator), cool, and reweigh the crucible and lid together. Repeat this process till the weight is constant. This shows that all the magnesium carbonate has been converted into magnesium oxide (with loss of carbon dioxide). Enter your results thus:—

---

* Use a filter paper the weight of the ash of which is known. Packets of such filter papers, with the weight of the ash marked outside, can be obtained.

grammes.
Weight of magnesium ... ... =
,, crucible, and lid ... ... =
,, ,, lid, magnesium oxide, and ash (1) =
,, crucible, lid, magnesium oxide, and ash (2) } constant (say) =
,, crucible, lid, magnesium oxide, and ash (3) } constant (say)
,, magnesium oxide ... ... =
,, oxygen combined with one part by weight of magnesium ... ... =

You will find that the result is the same as in Exp. 65 (*a*), *i. e.* whether magnesium oxide is made as in Exp. 65 (*a*) or in Exp. 65 (*b*) its composition is the same.

Exp. 66.—Composition of Chalk.—Powder some of the purest chalk you can get and place it in a weighed crucible, and obtain the combined weight of crucible *plus* chalk. Now heat strongly with a blowpipe flame for quite a long time. Allow to cool, and weigh again. It will now weigh less than before. Repeat the heating and weighing till there is no change in weight. Be careful to direct the flame against the bottom of the crucible. The total loss should be about 44 per cent.

This, as we know, represents the *carbon dioxide* which is driven off by heat; the residue is the *quicklime*.

Repeat the experiment with a different weight of chalk. You will again find that the loss in weight is 44 per cent.

Chalk, then, is composed of carbon dioxide and lime *combined in fixed proportions.*

Exp. 67.—Composition of Water.—Take a hard glass tube about 20 cms. long and 1·5 cms. wide, and fit it with corks. Push into the tube a loose plug of asbestos (which has been previously ignited and allowed to cool in a desiccator) so that it is about a quarter of the way up the tube (A, Fig. 18).

Weigh out, approximately, 5 grammes of finely-powdered black oxide of copper,[*] and introduce it into the tube at the end remote from the asbestos, by means of a small funnel. Now introduce a second plug of asbestos (ignited as before), carefully pushing it up the tube so that it sweeps along all particles of oxide. The distance between the two asbestos plugs should be about 6 cms. Place the tube horizontal and tap it so that the oxide forms an even layer with a free air space all along the tube. Carefully wipe off any oxide from the outside of the tube.

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[*] This should be previously heated to redness in air (to get rid of moisture, etc., attached to it), and, whilst still warm, introduced into the tube just before commencing the experiment.

Next weigh the tube and copper oxide accurately. Also weigh a U-tube containing granular calcium chloride, and united with a horizontal bulb as shown in the diagram. Attach the U-tube and bulb to the straight tube as shown (arranging that the tube which passes through the cork *does not reach beyond it.**) Connect the other end of the tube to a supply of hydrogen prepared by the action of dilute sulphuric acid on zinc, and dried by passing through a U-tube filled with granular calcium chloride. Allow the hydrogen to pass through the tube for a few minutes in order the displace the air. (Test if the air has been removed in the usual way.) Then heat the oxide of copper by means of a flat-flame burner. The colour of the oxide of copper will slowly change to a dark red, and water will be seen to condense in the further end of the tube and the horizontal bulb. The heating must be continued and the stream of hydrogen passed until no more traces of moisture are observed in the straight tube. You will find it necessary to warm the further end of the tube in order to drive out the water which collects there. Do this with an ordinary Bunsen burner, taking care that the tube does not become so hot as to affect the cork. Most of the moisture will now collect in the horizontal bulb, and the rest will be absorbed by the calcium chloride.

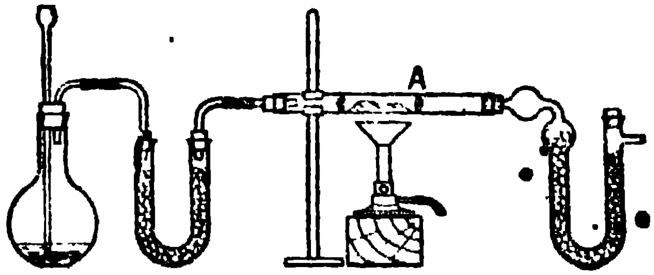

FIG. 18.

Now allow the apparatus to cool, still passing a slow current of hydrogen. When cold disconnect the hydrogen generating flask, leaving the calcium chloride tube in place. Now pass a slow current of dry air through the apparatus by means of the arrangement shown in Fig. 19.† The upper bottle A is filled with water, which flows down into B when the tap D and screw-clip C are open, and forces the air out through the exit-tube. The air is first passed through a small sulphuric acid wash-bottle E, which serves to indicate the rate of flow and also partially dries it. It then traverses the remainder of the apparatus (being further dried by the calcium chloride in the **U**-tube), and sweeps out the hydrogen.* The current of air is regulated by the tap and screw-clip, and should be maintained for about five minutes.

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* If it did you would be unable subsequently to drive all the water out of the tube.

† A simpler way is to use a "*scent bottle*" *bellows*.

Reweigh the tube (+ copper) and the **U**-tube and bulb. We have now all the data necessary for calculating the ratio of hydrogen to oxygen in water.

Enter your results thus :—

grammes.
Weight of heating tube + copper oxide ... ... $= x$
,, ,, ,, + copper ... ... $= y$
,, oxygen which has been converted into water ... ... $= x - y$
,, **U**-tube and bulb before experiment ... $= a$
,, ,, ,, ,, after ,, ... $= b$
,, hydrogen in the water formed ... ... $= b - a - (x - y)$

Hence-

Weight of oxygen united with 1 gramme of hydrogen is $\frac{x-y}{b-a-(x-y)}$.

You should find this to be about 8 grammes.

Repeat the experiment and show that you get the *same result.*

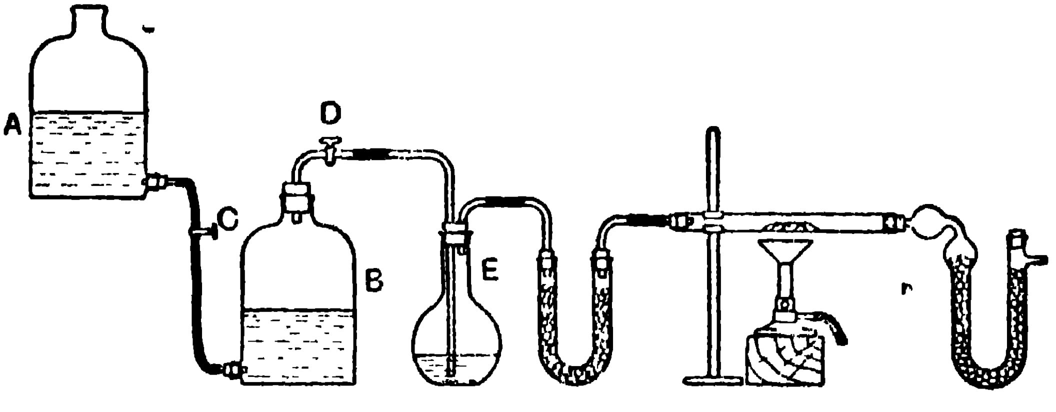

FIG. 19.

Now try another oxide in place of copper oxide—say litharge ; again the result will be the same.

A very large number of experiments have been made similar to those you have just performed, and all have led to similar results, which may be generalised in the following statement known as the *Law of Constant Proportion* :—

---

* If you weigh with hydrogen in the tubes instead of air, you will introduce errors ; for the previous weighings were made with air in the tube, and hydrogen is much lighter than air.

The same compound always contains the same elements combined in the same fixed proportion by weight.

Here, then, we have a very important characteristic of a *chemical compound*, for in a *mixture* the constituents may be present in *any proportions*.

47. Law of Multiple Proportion.—Many elements, however, are capable of combining together to form more than one compound. Let us now perform some experiments with a view to finding out whether in two compounds of the same elements there is any simple relation between the relative proportions of these elements.

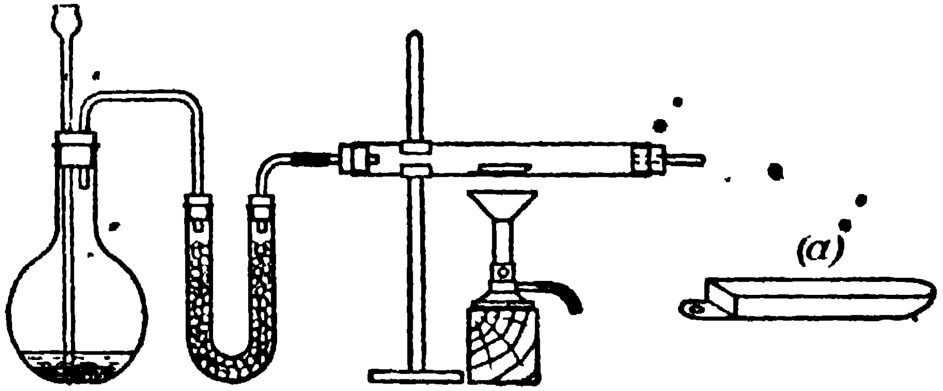

FIG. 20.

Exp. 68.—Weigh accurately into a small porcelain boat (*a*, Fig. 20) about a gramme of puce-coloured oxide of lead. Push the boat into a hard glass tube of about the same size as that used in Exp. 67. Fit the tube with corks, carrying short pieces of glass tubing. Now connect one end of the tube with an apparatus for preparing dry hydrogen. Allow the hydrogen to pass through the tube for a few minutes to displace the air (test as usual). Then heat the boat gently by means of a flat flame burner. The powder gradually changes colour, while *steam* passes out of the tube along with the unused hydrogen. When the cloud ceases and the powder has become quite black (*i. e.* changed into metallic lead) raise the boat to red heat for a few seconds to fuse the lead, while the current of hydrogen still passes. Cool, stop the current of hydrogen, withdraw the boat by means of a copper wire from the end of the tube attached to the hydrogen apparatus (because there will probably be some drops of water at the other end) and reweigh it.

Enter your results thus:—

grammes.
Weight of boat + puce oxide of lead . . .. $= x$
,, boat ... ... $= y$
,, boat + lead ... ... $= a$
,, lead in oxide taken ... . $= a - y$
,, oxygen in oxide taken ... ... $= x - a$

Therefore the weight of lead combined with one part by weight of oxygen in puce oxide of lead is $\frac{a-y}{x-a}$ grammes.

Your result should work out at about 6·45 grammes.

Now repeat the experiment, using litharge (yellow oxide of lead) instead of puce oxide of lead, and again calculate out the weight of lead which was in combination with one gramme of oxygen. The weight found should be about 12·9 grammes.

Now $6{\cdot}45 : 12{\cdot}9 = 1 : 2$, *i. e.* the weights of lead which unite with 1 gramme of oxygen to form puce oxide of lead and litharge respectively are in the ratio $1 : 2$.

There is then a very simple relation between the relative weights of oxygen which combine with a fixed weight of lead to form these two oxides of lead.

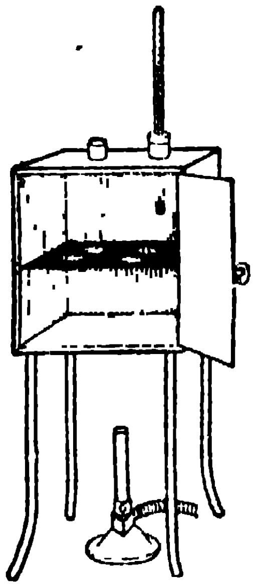

FIG. 21.

Exp. 69.—Clean and heat a porcelain crucible and lid, and allow them to cool. Place in the crucible about 1 gramme of well-powdered recrystallised copper sulphate crystals, and accurately weigh the whole. Heat, with the lid off, for half-an-hour in an air oven (Fig. 21) kept at a temperature of 135° C. to 140° C. Stir the powder occasionally with a platinum wire. When properly heated it should appear whitish all through. Allow the crucible to cool with its lid on, and weigh again. The difference in weight gives the weight of water lost.

Next support the crucible on a pipeclay triangle, and heat it very carefully (without the lid), using a small flame, which is not allowed to touch the crucible. Cool with the lid on, and weigh. The heating and cooling should be repeated until practically a constant weight is obtained, when all water will have been expelled. The difference between this weight and the former shows the loss of water due to the raised temperature. It should be just one quarter of the first loss.

The results obtained by a student were as follows:—

	grammes.
Weight of crucible, lid, and powdered crystals	13·727
,, crucible, lid, and powdered crystals after heating to 140° C.	13·440
,, water expelled at lower temperature	0·287
,, crucible, lid, and anhydrous copper sulphate ..	13·367
,, water expelled at higher temperature	0·073
Total weight of water in the crystals	0·360

Thus the proportion of water in the crystals to that in the first product was found to be 0·360 : 0·073, or 5 : 1, or, in other words, the weights of water which unite with a fixed weight of copper sulphate to form two different compounds bear to one another the simple ratio 5 : 1.

Similar experiments with other substances have led to similar results. Thus:—

12 gms. of carbon combine with 16 gms. of oxygen to form carbon monoxide.
12 gms. of carbon combine with 32 gms. of oxygen to form carbon dioxide.

Ratio between the weight of oxygen combining with the same weight of carbon is 1 : 2.

32 gms. of sulphur combine with 32 gms. of oxygen to form sulphur dioxide.
32 gms. of sulphur combine with 48 gms. of oxygen to form sulphur trioxide.

Ratio between the weights of oxygen combining with the same weight of sulphur is 2 : 3.

These and all similar cases may be summed up in the following statement, which is known as the *Law of Multiple Proportion*:—*When one element combines with another in more than one proportion the different quantities of the one element which unite with a fixed quantity of the other element bear a simple ratio to one another.*

QUESTIONS.—CHAPTER VII.

1. Describe two experiments to illustrate the truth of the statement that matter can neither be created nor destroyed.
2. In what respects does a chemical compound differ from a mixture? Describe experiments to illustrate your answer.
3. State the *Law of Constant Proportion*, and describe how you would proceed to demonstrate its truth by experiment.
4. What is the *Law of Multiple Proportion?* Describe experiments which illustrate it.
5. Show that the following numbers illustrate the Law of Multiple Proportion:—Red oxide of copper contains 88·8 per cent. of copper and 11·2 per cent. of oxygen. Black oxide of copper contains 79·87 per. cent. of copper and 20·13 per cent. of oxygen.
6. Show that the following numbers illustrate the Law of Constant Proportions:—2·4 grammes of oxide of iron on complete reduction by hydrogen yielded 1·68 grammes of iron; 2·9 grammes of the oxide yielded on similar treatment 2·03 grammes of iron.
7. What do you understand by the *Principle of the Conservation of Matter?* Describe how you would proceed to illustrate the truth of this principle by experiment.
8. You are provided with a powder containing copper and sulphur in the proportions of 63 : 32. Describe how you would proceed to find out whether it is a mixture or a compound of the two elements.

CHAPTER VIII.

PHYSICAL PROPERTIES OF GASES

48. **Effect of Temperature on the Volume of a Gas.**—You have already observed (Exp. 6) that air expands when heated and contracts when cooled, and you would find a similar result with other gases. Let us now examine this phenomenon quantitatively by experiment.

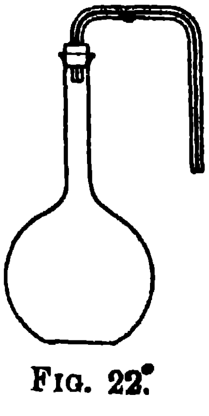

FIG. 22.

Exp. 70.—Relation of volume of air to temperature.—Take a 250 c.c. flask and tightly-fitting indiarubber cork, through which passes a piece of glass tubing of very narrow bore (capillary tubing), bent twice at right angles as shown in Fig. 22. Immerse the flask up to the level of the cork in a beaker or tin vessel of hot water, clamping it in position so that there is, say, half-an-inch of water between the bottom of the flask and the beaker. Boil the water and keep it boiling for some five or ten minutes. Now place a beaker with cold water so that the outlet of the capillary tube dips deeply into it. Raise the flask out of the hot water, keeping the outlet all the while dipping beneath the water in the beaker, and let it cool by standing in the air. Notice that water is driven from the beaker into the flask. Plunge the flask overhead into a mixture of water and ice, still keeping the outlet under water, and let it remain so long as water drips back into it through the capillary tube. Take now a cylindrical measure graduated into cubic centimetres, and pour the water from the flask into it so as to ascertain how many cubic centimetres have flowed back into the flask. Call this v. Then measure how much water is needed to fill the flask up to the level of the lower surface of the cork. Call this V. Then V represents the volume of air which just fills the flask at 100° C. and $(V - v)$ the volume which this air occupies at 0° C., the temperature of ice-cold water. Therefore $(V - v)$ c.cs. of air at 0° C. expand v c.cs. on heating to 100° C.

The amount of expansion for 1° C. rise in temperature is $\frac{v}{100}$ c.cs.; therefore the expansion for 1° is $v \div (V - v)$ 100 of the whole. Calculate out from your results the value of this expression, and see how near it agrees with the number $\frac{1}{273}$.

John Dalton, who in 1801 made this determination, and found that oxygen, hydrogen, and carbonic acid gas behaved in the same manner as air, obtained the result $\frac{1}{275}$. He concluded "that all elastic fluids under the same pressure expand equally by heat."

This generalisation is, however, usually known as *Charles's Law*, which is expressed thus:—

Equal volumes of all gases under the same pressure expand equally for equal increments of temperature.

Experiments in which precautions were taken to secure great accuracy yield the result that gases at 0° C. expand $\frac{1}{273}$ part of their volume for each increment of 1° C.

Thus 273 volumes of gas at 0° C. become 274 vols. at 1° C.,
,, ,, ,, 275 vols. at 2° C.,
,, ,, ,, 276 vols. at 3° C.,
and so on.

For temperatures below zero, we should have—
273 volumes of gas at 0° C. become 272 vols. at − 1° C.,
,, ,, ,, 271 vols. at − 2° C.,
,, ,, ,, 270 vols. at − 3° C.,
and so on.

If the behaviour of gases remained the same at *very low* temperatures, we should find that 273 vols. at 0° C. would become *nil* at − 273° C. But, long before such a low temperature is reached, most gases condense to liquids, and many even to solids.

In dealing with gases in practice, however, the chemist has usually only to concern himself with temperatures above zero and a few degrees below zero; and hence you will find it convenient to notice that *under the same pressure the volume of a gas is proportional to the temperature as reckoned, not from 0° C., as is generally done, but from* – 273° C., termed *absolute zero.* We have thus:—

Temperature.	Absolute Temperature.	Volume.
0° C.	273	273
10° C.	283	283
-10° C.	263	263

and so on.

49. **Effect of Pressure on the Volume of a Gas.**—A simple experiment with a pop-gun will convince you that the volume of space taken up by a gas depends also on its pressure. The effect can be investigated quantitatively by means of the following experiment.

Exp. 71.—Take a dry glass tube of not less than 5 mms. bore and ½ metre in length. Near one end draw it out to a fine orifice in the following manner:—Heat in a small blowpipe flame until a short length (about 5 or 10 mms.) is quite soft, and then rapidly draw it apart. In this way the tube will be of the same diameter very nearly up to the orifice. [Why should it be so?] Now attach the other end of the tube firmly to a length of at least a metre of thick-walled india-rubber tubing ("pump tubing"), and at the other extremity of the rubber tubing a funnel or receptacle of the form shown in Fig. 23. Fix the receptacle at a level about halfway up the glass tube, and pour in mercury, taking care that no bubbles of air are entrapped. Now, by means of a small flame, seal up the orifice of the glass tube and allow it to stand for a few moments; then mark with a narrow slip of paper the level at which the mercury stands on the tube.

Carefully measure the length of the tube containing air, and record this, = A. The pressure under which the air at present stands is that of the atmosphere, and equal to the reading of the barometer for the time being, = P. Record this. Raise the receptacle about half-a-metre, and note how the column in the tube also advances. Mark the level at which it stands with a second strip of paper, and measure the distance from it to the top of the tube, = B; also measure the height at which the mercury in the receptacle stands above that of the second strip of paper, = p. Repeat these operations when you have brought the receptacle to the level of the table or even lower, recording the length of the air column as C and the measure of the level of the mercury in the receptacle *below* that of the column in the glass tube as p'. Assuming the tube to be of even bore throughout, and that the temperature has remained constant, the volume of the air in the tube at the three periods recorded will be in the proportion $A : B : C$, and the pressure under which the air is will be $P : P + p : P - p'$.

See now how far your records support the following statement, known as *Boyle's Law*:—

When the temperature remains constant the volume occupied by a gas varies inversely as the pressure.

Note also that, this being the case, the product of the volume and the pressure will be constant, and see from your records if you find

$$A \times P = B \times (P + p) = C \times (P - p').$$

Indicating pressure by P and volume by V we have then

$$PV = \text{a constant.}$$

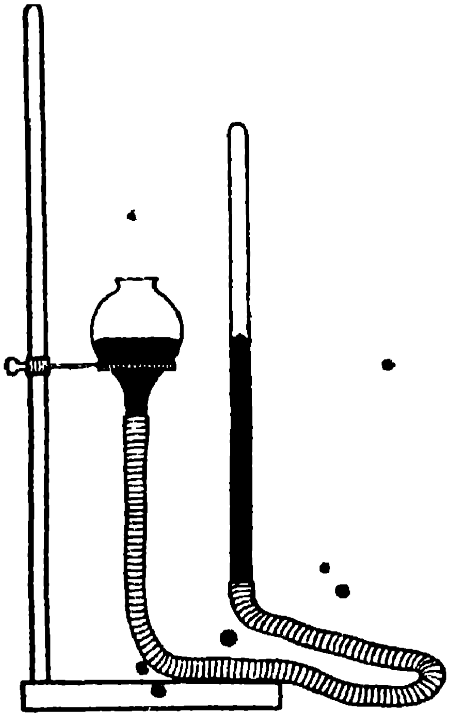

FIG. 23.

50. Liquefaction of Gases.—The above description is only true for a perfect gas under moderate pressure and temperature. No perfect gas exists in reality, for though very many gases show a close agreement at such pressures and temperatures as occur in general practice, yet under extreme conditions even hydrogen, nitrogen, and those gases which behave most nearly like perfect gases, fail to show agreement, and at sufficiently low temperature and high pressure they change their condition and become liquid.

The following table gives the temperatures and pressures at which some of the commoner gases become liquids:—

Carbon dioxide at	− 80° C.	and	1	atmosphere	pressure
or at	+ 20° C.	„	58	„	„
Sulphur dioxide at	− 10° C.	„	1	„	„
or at	+ 10° C.	„	2·3	„	„

Air at — 194·4° C. and 1 atmosphere pressure
or at — 140° C. ,, 39 ,, ,,
Chlorine at — 34° C. ,, 1 ,, ,,
or at 0° C. ,, 6 ,, ,,
Nitrous oxide at 0° C. ,, 30 ,, ,,

Various methods have been employed in liquefying gases. Faraday was able to liquefy a large number of gases by means of their own pressure in glass tubes. To liquefy chlorine in this way a quantity of the yellow crystals of chlorine hydrate (a compound of chlorine and water) are brought into a glass tube of about 1 cm. in diameter, and closed at one end. The tube is then bent at right angles at about its middle point, and sealed. If now the sealed end be placed in a freezing mixture, whilst the other end containing the hydrate be gently warmed, a comparatively large volume of chlorine is liberated, and the pressure of the accumulated gas together with the low temperature employed is sufficient to bring about its liquefaction.

If silver chloride be saturated with ammonia gas, a compound of the two is formed, and this body treated in the same way evolves ammonia in such a quantity as to liquefy by its own pressure.

With many gases a much lower temperature is required than can be obtained by using an ordinary freezing mixture. Thus Pictet liquefied oxygen by submitting it to a very high pressure in a copper tube at — 140° C.

51. To measure the Volume of Carbon Dioxide evolved from one gramme of Chalk.—

Exp. 72.—Take a large bottle (a Winchester quart) and fit it with a cork carrying two delivery tubes bent at right angles, one long enough to reach nearly to the bottom of the bottle, the other quite short (see Fig. 24). The longer delivery tube should be attached to another similar tube by a piece of rubber tubing on which a clip is placed. Nearly fill the bottle with water and pour on the top a few c.cs. of paraffin oil. Introduce the cork, blow through the short delivery tube till water runs out of the long tube (which constitutes a siphon tube), then tighten the clip. Now procure a small wide-mouthed flask and fit it with a cork, and short delivery tube bent at right angles. Weigh the flask, introduce about a gramme of chalk, and weigh again. The difference between the two weighings gives you the weight of chalk taken.

Now add a little water, and then carefully introduce a small tube nearly filled with strong hydrochloric acid, leaning it up against the side of the flask. Insert the cork, and connect the delivery tubes of the flask and the bottle by a short piece of rubber tubing.* Place the free arm of the siphon in a tall graduated cylinder. Open the clip. A few drops of water escape and then the flow should cease; if it does not do so then air is finding its way into the apparatus, *i. e.* the corks are not tight. Close the clip, push all the corks well home and test again.

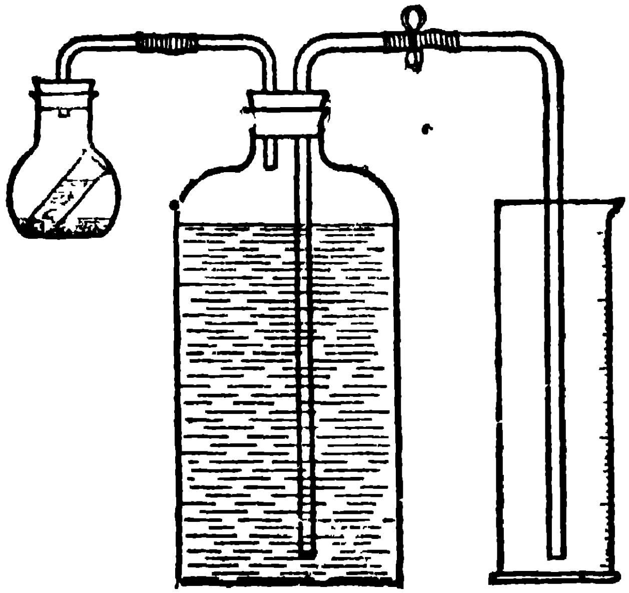

FIG. 24.

When the apparatus is gas-tight† incline the flask until a little of the liquid runs over on to the chalk, repeating the operation from time to time so long as effervescence continues. The carbon dioxide evolved pushes air over into the bottle, and this in its turn displaces water, which passes over into the cylinder. In time carbon dioxide reaches the bottle but is prevented from dissolving in the water by the layer of oil. At the end of the experiment allow the apparatus to remain for a few minutes in order that it may regain atmospheric temperature. Gently agitate the liquid in the flask occasionally.

---

* By this arrangement the pressure of the air in the apparatus at the commencement of the experiment is atmospheric.

† If a measurable quantity of water has collected in the cylinder you must read off the volume and subtract it from the final volume.

Next make the levels of the liquids in the cylinder and bottle the same by raising or lowering the cylinder (so making the pressure in the apparatus atmospheric), close the clip, remove the siphon tube from the cylinder, and read the volume of water in the latter. This represents the volume of gas which has passed into the bottle, and so the volume of carbon dioxide evolved from the chalk taken, measured at the temperature and pressure of the atmosphere.

Suppose in an experiment the following results were obtained :—

Weight of flask + chalk = 10·364 gms.
,, ,, alone = 9·134 ,,
,, chalk taken = 1·230 ,,

Volume of water collected = 287 c.cs.

Then we have—

1·23 grammes of chalk yield 287 c.cs. of carbon dioxide.

Therefore—

1 gramme of chalk would yield $\frac{287}{1\cdot 23}$ or 233 c.cs. of carbon dioxide measured at the temperature and pressure of the atmosphere.

Now we have seen that the volume of a given quantity of gas varies with both the pressure and the temperature. But the temperature of the laboratory and the pressure of the surrounding atmosphere vary from day to day and from place to place, so that some one else working with quite as great accuracy might obtain a volume of gas somewhat different from yours. In order therefore that results may be compared together, we must all agree to state our results as they would be if they were all performed under the same conditions as to temperature and pressure, and it has been agreed that the temperature for such reference shall be the freezing-point of water (0° C.), and the normal or average pressure of the atmosphere, equal to that of a column of mercury 760 millimetres in height. These standard conditions are referred to as "Normal temperature and pressure," and the expression is often abbreviated to the letters "N.T.P."

Suppose that when you performed your experiment the temperature of the atmosphere was 15° C. and the pressure

775 millimetres of mercury. Let us reduce the volume of gas evolved to standard conditions. We have—

$$0° \text{ C.} = 273° \text{ absolute.}$$
$$15° \text{ C.} = 273 + 15 \text{ or } 288° \text{ absolute.}$$

Therefore by Charles' Law the volume will be decreased in the ratio $\frac{273}{288}$ when reduced to 0°.

Again by Boyle's Law the volume will be increased in the ratio $\frac{775}{760}$ when reduced to 760 millimetres.

Applying both corrections we have for the volume at 0° C. and 760 millimetres—

$$233 \quad \frac{273}{288} \times \frac{775}{760} \text{ or } 225 \text{ c.cs.}$$

An apparatus similar to that described above may be employed for finding the volume of hydrogen evolved when metals such as zinc and magnesium are treated with sulphuric or hydrochloric acid. In this case the layer of oil is not required, as hydrogen is practically insoluble in water.

52. To measure the Mass of Carbon Dioxide evolved from one gramme of Chalk.—

Exp. 73.—Take a small wide-mouthed bottle and fit it with a rubber cork carrying a drying tube filled with granulated calcium chloride and a glass tube reaching nearly to the bottom of the bottle (see Fig. 25). Accurately weigh out into the flask about 1 gramme of chalk. Pour water into the bottle till the chalk is well covered. (Do not add too much water.) Next tie a piece of cotton underneath the rim of a small test-tube, nearly fill the tube with strong hydrochloric acid, and lower it into the bottle. Now without leaving hold of the cotton insert the cork, so arranging that when the cotton is held tight by the cork the tube is in the position shown in the figure. See that the end of the straight tube dips in the liquid.

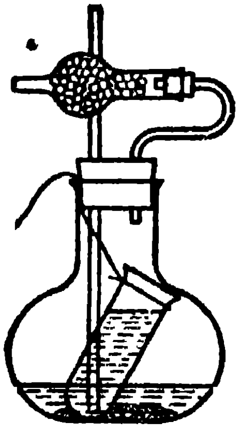

FIG. 25.

Now carefully weigh the whole. Then manipulate the bottle so that a *little* acid escapes from the small tube on to the chalk. Carbon dioxide is evolved, and first drives air out of the flask through the calcium chloride tube (its only exit); after a time the gas itself passes out. Any moisture carried away by the escaping gases is retained by the calcium chloride, and so loss in weight is prevented. (If, however, the action is allowed to proceed *too rapidly* the drying will not be carried out effectively.) When the action slackens upset a little more acid, and continue to do this from time to time till all the chalk has disappeared.

The flask is now full of carbon dioxide, and further, some of the gas is dissolved in the liquid. Warm the flask carefully till it is so hot that you can barely hold it. (*Do not boil the liquid.*) Now attach a piece of rubber tubing to the calcium chloride tube and suck *gently* till the pungent taste of carbon dioxide ceases to be noticed. The flask is now full of air again. Allow it to stand till it becomes quite cold, and then reweigh.

Suppose the following results were obtained :—

Weight of flask + chalk = 10·321 gms.
,, ,, alone = 9·136 ,,
,, chalk taken = 1·185 ,,

Weight of apparatus before the reaction = 35·614 gms.
,, ,, after ,, ,, = 35·087 ,,
,, carbon dioxide evolved = 0·527 ,,

We have then—

0·527 gramme of carbon dioxide is evolved from 1·185 grammes of chalk.

Therefore—

$\frac{0.527}{1.185}$ or 0·445 gramme of carbon dioxide is evolved from 1 gramme of chalk.

53. Density of Gases.—By the *density* of a gas we mean the *mass of it which occupies unit volume.* The most convenient volume to take as the unit is 1 *litre.* A very simple experiment will convince you that the densities of different gases vary very much.

Exp. 74.—Take a large beaker and suspend it from one arm of a rough balance. Add weights to the other scale-pan till the balance is in equilibrium. Now prepare some carbon dioxide and pour it into the beaker; the arm to which the beaker is attached at once *sinks,* showing that carbon dioxide has a greater density than air.

Now repeat the experiment, but hang the beaker in an inverted position and pour hydrogen *up* into it; the arm to which the beaker is attached *rises,* showing that the density of hydrogen is less than that of air.

Since hydrogen is the least dense of all gases it is very common to state the *relative density* (or specific gravity) of a gas in terms of hydrogen as unity, instead of stating the density as defined above. The *relative density* of a gas (in terms of hydrogen as unity) may by defined as the *weight of a given volume of the gas divided by the weight of an equal volume of hydrogen under the same conditions of temperature and pressure.*

Sometimes relative densities are given in terms of *air* as unity.

Density of Air.—The density of air may be determined approximately in the following manner:—

Exp. 75.—Fit a strong flask, holding about 300 c.cs., with a cork through which passes a short length of glass tubing. Attach to it a piece of rubber tubing carrying a clip. Place about 30 c.cs. of water in the flask, open the clip, and boil the water for ten minutes. The steam drives out all the air. Close the clip, remove the flame at once, allow to cool, and weigh the flask and its contents (w_1).

Now open the clip carefully so as to allow air to enter gradually. [Why does air enter?] When no more air enters weigh again (w_2), and measure the volume of water that remains (v_1). Finally, fill the flask with water to the level of the cork, and measure the volume of this water (v_2).

Let t° be the temperature of the air.

Let H be the barometric height in millimetres of mercury.

$(v_2 - v_1)$ c.cs. is the volume of air at t° and H millimetres that (together with the v_1 c.cs. of water) filled the flask.

$(w_2 - w_1)$ grammes is the weight of this air.

The volume at N.T.P. is $(v_2 - v_1) \times \frac{H}{760} \times \frac{273}{273 + t} = v$ say.

Therefore the mass of 1 litre at N.T.P. is $\left(\frac{w_2 - w_1}{v} \times 1000\right)$ gms.

Calculate out your result and see how near it agrees with the value 1·293 grammes, which accurate measurements have shown to be the correct density of dry air. [Your result cannot be quite correct because the air filling the flask is *moist*, not *dry*; but at this stage you had better not trouble about the correction.]

Density of Carbon Dioxide.—You can calculate this roughly from the results of Exps. 72, 73, for in Exp. 72 you have found the *volume* of carbon dioxide evolved from 1 gramme of chalk, and in Exp. 73 the *mass* of the gas evolved from 1 gramme of chalk.

By Exp. 72—

1 gramme of chalk gave 225 c.cs. of carbon dioxide measured at N.T.P.

By Exp. 73—

1 gm. of chalk gave 0·445 gramme of carbon dioxide.

∴ 225 c.cs. of carbon dioxide measured at N.T.P. weigh 0·445 gramme.

∴ 1000 c.cs. or 1 litre of carbon dioxide measured at N.T.P. weigh $1000 \times \frac{0·445}{225}$ or 2 gms.

Now 1 litre of hydrogen has been found to weigh 0·09 gramme; therefore the density of carbon dioxide relative to hydrogen is about $\frac{2}{0·09}$ or 22.

Density of Oxygen.—We can determine the density of oxygen by a method somewhat similar to that which we have used in the case of carbon dioxide, namely by finding (*a*) the mass, (*b*) the volume of oxygen evolved on heating 1 gramme of potassium chlorate.

(*a*) *To estimate the mass of oxygen evolved on heating* 1 *gramme of potassium chlorate.*

Exp. 76.—Weigh a small hard glass tube, place in it about 1 gramme of potassium chlorate and weigh again. Heat carefully, holding the tube in a slanting position and rotating it constantly. The salt melts and then appears to boil. The gas evolved rekindles a glowing splinter at once.

After a time the liquid gets thick, and when the gas evolution ceases a white and solid mass (potassium chloride) remains in the tube.

Weigh the tube again when cool, and calculate the weight of oxygen which would be evolved from 1 gramme of potassium chlorate. The result should be about 0·39 gramme.

In a similar way the weight of oxygen evolved from 1 gramme of nitre or red lead may be found.

(*b*) *To estimate the volume of oxygen evolved on heating* 1 *gramme of potassium chlorate.*

Exp. 77.—Fit up an apparatus similar to that described in Exp. 72, but replace the small bottle by a hard glass tube containing about 1 gramme of potassium chlorate (accurately weighed out). After filling the siphon tube as described in Exp. 70, attach the hard glass tube and test if the apparatus is air-tight. When it is so, heat the potassium chlorate. The oxygen evolved displaces the water from the bottle, and the water runs into the cylinder. When the level of water in the latter ceases to rise, allow the tube to cool to the temperature of the air. This will have happened when the level of water in the cylinder ceases to *fall*. Now make the levels of water in the cylinder and bottle the same, close the clip and remove the siphon tube. Read the volume of liquid in the cylinder: this is the volume of oxygen evolved from the weight of potassium chlorate taken measured at the pressure and temperature of the atmosphere.

From your result calculate the volume of oxygen at N.T.P. which would be evolved from 1 gramme of potassium chlorate. It should be about 270 c.c.

From the results of Exps. 75, 76 calculate the density of oxygen just as you did that of carbon dioxide. You should find that a litre of oxygen weighs about 1·4 grammes.

54. Diffusion of Gases.—

Exp. 78.—Pour a little "liquor ammonia"* (an aqueous solution of the gas ammonia) into a basin, and leave it standing in the middle of the room. Very soon you will find that the smell has permeated to all parts of the room.

Exp. 79.—Procure a tall narrow gas jar and pass into it some carbon dioxide, letting the delivery tube reach quite to the bottom of the jar. If you first burn a little brown paper in the jar you will be able to see how the heavier carbon dioxide collects in the bottom of the cylinder, almost as a liquid would, pushing the air out above it. Fill the jar in this way about one-third and then lift out the delivery tube, pinching it so that no gas may pass into the upper part of the jar while you are raising it. Cover the mouth of the jar with a glass plate and set it aside for an hour. After this interval plunge a lighted taper into the jar and lower it until you reach a level where it is extinguished.

Mark the level and compare it with that at which the carbon dioxide originally stood. You will find that the level has risen.

Now by means of a syringe withdraw some of the gas from the bottom of the jar. Fill a test-tube with caustic soda solution, invert it in a trough of water and support it by means of a clamp. Place the syringe in the water and force gas out of it into the test-tube till the latter is about two-thirds full. Next place your thumb over the mouth of the tube, remove it from the trough and shake up vigorously. Invert the tube in the water again and remove your thumb. The water rises but does not completely fill the tube, showing that the gas was not all carbon dioxide.

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* Also called "liquid ammonia." Be careful not to inhale much of the vapour rising from the liquid, as it is injurious.

Test the unabsorbed gas with a lighted taper. The taper continues to burn; the gas is air.

If the jar were left long enough it would be found that the air and carbon dioxide had become uniformly mixed throughout.

Exps. 78, 79 illustrate a general property of gases, namely, that they ultimately spread—or *diffuse*—to the boundaries of any closed space into which they are introduced, however large the space. The spreading or *diffusion* of a gas takes place independently of the presence of other gases, and consequently, however many different gases are introduced into a closed space, ultimately they will all be distributed homogeneously throughout that space.

The phenomenon of gaseous diffusion is in apparent contradiction to the law of gravitation, for if, as in Exp. 79, we start with the heavier of two gases (carbon dioxide) below and the lighter (air) above, the heavier gas passes *upwards* and the lighter *downwards*.

The explanation of the phenomenon is that the very small particles of which gases are composed are in constant rapid motion in directions which are continually changing, owing to collisions with other particles, or with the walls of the containing vessel. [It is the bombardment of the particles on the walls of the vessel which gives rise to gaseous pressure.] It will now be seen that gaseous diffusion does not really contradict the law of gravitation, for, to return to Exp. 79, at any given instant some particles of carbon dioxide are moving upward in opposition to gravity just as a cricket-ball does when thrown up into the air.

It is this property of gaseous diffusion which explains the fact that mixtures of gases of different density do not separate into layers with the heaviest gas at the bottom and the lighter ones above in order of decreasing density. Air, for example, is a homogeneous mixture of oxygen and nitrogen; it does not separate into two layers, oxygen, the heavier gas, below, and nitrogen, the lighter gas, above.

Graham's Law of Gaseous Diffusion.—Let us now try to discover whether all gases diffuse at equal rates or whether on the other hand there is (as we might rather expect) some relation between the density of a gas and the rate at which it diffuses.

Exp. 80.—A porous cell, such as is used in voltaic batteries, is fitted with an indiarubber stopper, and a glass tube about half a metre long, furnished with a bulb, is passed through the stopper; this is bent and drawn out into a jet as shown in Fig. 26. Before inserting the cork fill the bulb and lower part of the tube with water. Now place a beaker filled with hydrogen over the porous cell, and the water will be immediately depressed and driven out of the jet in a fine stream.

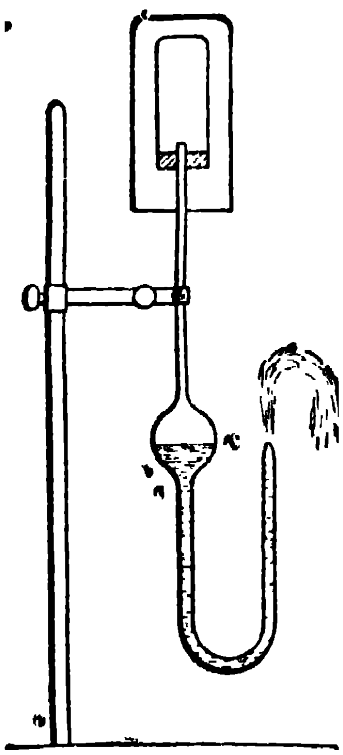

Fig. 26.

This is evidence that the light gas hydrogen passes through the walls into the porous cell quicker than the air is able to pass out of it. A greater volume of gas collects within the space of the cell and tube and forces the water out before it.

By slightly varying the experiment it may be shown that carbon dioxide, which is heavier than air, diffuses less rapidly. Graham, who performed a number of quantitative experiments on diffusion, found that *the relative rates of diffusion of gases are inversely proportional to the square root of their densities.* This statement is known as *Graham's Law of Gaseous Diffusion.*

Thus in relation to air:—

		$\frac{1}{\sqrt{\text{density}}}$	Velocity of diffusion observed.
Density of hydrogen	= 0·0695	= 3·792	3 830
„ carbon dioxide	= 1·5180	= 0·812	0·812

N.B.—For questions on Chapter VIII. see page 108.

CHAPTER IX.

CHEMICAL EQUIVALENTS—THE ATOMIC THEORY—AVOGADRO'S HYPOTHESIS.

55. **Chemical Equivalents.**—In our investigation of the Law of Constant Proportion (Chap. VII.) we determined the composition of *water* (Exp. 67), and arrived at the following result:—

Water is composed of *hydrogen* and *oxygen*, in the proportion of 1 gramme of the former to 8 grammes of the latter.

We may say, therefore, that in water 1 gramme of hydrogen is *equivalent to* 8 grammes of oxygen.

Again, an investigation of the composition of oxide of zinc on the lines of Exp. 65 (*b*),* would show that 4·06 grammes of zinc unite with 1 gramme of oxygen.

We may say, therefore, that in oxide of zinc 4·06 grammes of zinc are *equivalent to* 1 gramme of oxygen, or in other words 4·06 × 8, or 32·5 grammes of zinc, are equivalent to 8 grammes of oxygen.

Now we have seen (§§ 29, 33) that zinc reacts with acids such as sulphuric and hydrochloric with replacement of the hydrogen of the acid by the metal. The question arises whether there is any connection between the weights of zinc and hydrogen, which are respectively equivalent to 8 grammes of oxygen (*i.e.* 32·5 grammes and 1 gramme) and the weight of zinc which displaces 1 gramme of hydrogen from an acid. Let us submit this to the test of experiment.

Exp. 81.—Take a long measuring tube closed at one end and graduated in cubic centimetres. One graduated up to 100 c.c. is preferable. Take a narrow beaker, pour in about half a litre of water, and add about 30 c.c. of concentrated sulphuric acid, stirring briskly. When cool fill up the tube completely with the acid, taking care that no air bubbles are allowed to enter; close the open end by means of the thumb, and invert in the beaker, which contains the greater portion of the diluted acid. Fix the tube in a small clamp stand.

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* The method of Exp. 65 (*a*) cannot be applied satisfactorily in the case of zinc.

Procure a small tube about 1½ in. long and of such a diameter that it will slide comfortably into the graduated tube. Next scrape a piece of zinc foil to remove all oxide, and weigh out a piece of about 0·25 gramme (it should not be more). Roll the foil up, introduce it into the small tube and add two or three drops of copper sulphate solution*; then fill up with water, shaking well to disengage any air bubbles. Close the end of the tube by means of the thumb, and bring it under the mouth of the graduated tube (which is still under the dilute acid). Force the small tube up into the wider one, and lower the latter until it almost touches the bottom of the beaker and completely encloses the other. Remove your hand and rinse off the acid. Soon the heavier acid will diffuse to the zinc and begin to dissolve it. Hydrogen will be evolved, and will be collected in the tube.

When the zinc has completely dissolved, adjust the tube so that the liquid inside is level with that outside, more water being poured into the beaker if necessary. Do not touch the tube with your hand, but let it remain in the clamp, upon which hang a thermometer close to the tube in order to read the temperature of the air in the neighbourhood of the gas.

In a few minutes read the volume of gas, the temperature, and the barometric pressure; and from these calculate the volume at 0° C. and 760 mm., making allowance for the fact that the gas is not dry, but is saturated with aqueous vapour.† In making the correction, use the table given in the Appendix. Knowing that a litre of hydrogen under these conditions weighs 0·09 gramme, find the weight of the hydrogen collected.

Then the weight of zinc which displaces 1 gramme of hydrogen is given by

$$\frac{\text{Weight of zinc taken}}{\text{Weight of hydrogen collected}}.$$

If the experiment has been carried out carefully it will be found that *32·5 grammes* of zinc displace *1 gramme* of hydrogen. Repetition of the experiment with a different weight of zinc would be found to lead to the same result, and we may say, therefore, that 32·5 grammes of zinc are equivalent to 1 gramme of hydrogen.

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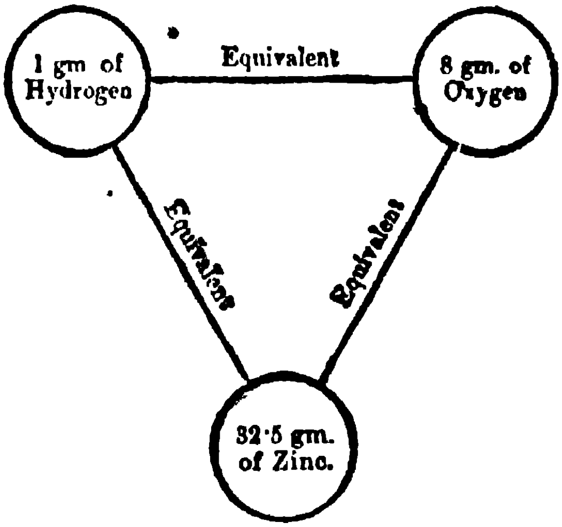
* Zinc in the form of foil would probably be so pure that it would not dissolve in sulphuric acid unless a little copper sulphate were added.

† This aqueous vapour exerts a pressure, and for a *given temperature* this pressure has a *definite value* if the gas contains as much aqueous vapour as possible, *i.e.* is *saturated* with it.

But we have seen above that these are the weights of the two elements which are respectively equivalent to 8 grammes of oxygen. We therefore arrive at the very striking result that the weights of zinc and hydrogen which are equivalent to a given weight of oxygen are the weights of these two elements which are equivalent to each other. This relationship is conveniently represented by a diagram:—



Now, just as in Exp. 81 the hydrogen was displaced from an acid by a metal, so it is possible to displace one metal from a salt by another metal (see Exp. 1). Let us investigate this process quantitatively.

Exp. 82.—Weigh accurately a rather deep porcelain crucible of about 50 c.c. content. Into this bring about 35 c.c. of a solution containing not less than 3·5 grammes of copper sulphate, and then about 0·4 gramme of zinc foil, the exact weight of which has been determined. Warm gently. The zinc will slowly disappear, and a heavy powder will be precipitated to the bottom of the vessel. When on stirring with a glass rod there is no longer any sign of the foil, the reaction is complete. The zinc has replaced the copper in the salt originally taken, and we have now in the vessel metallic copper and a solution containing zinc sulphate and excess of copper sulphate. In the meantime fold a filter paper and fit it into a funnel. Remove it, roll it up and introduce it into a wide test-tube, the upper half of which has been cut off. Place the tube in an air oven (Fig. 21, p. 68) and regulate the temperature to about 110° C. After about half-an-hour allow the tube to cool in a desiccator and weigh. Heat up again, allow to cool and reweigh. Repeat this process till the weight is constant.

Now place the filter paper in the funnel, filter off the precipitate of copper, and wash with hot water till a drop of the wash water gives no blue coloration with ammonia. Wash with alcohol two or three times and dry in the air oven. Next roll up the filter paper with the precipitate inside, place it in the tube and weigh. Repeat the drying and reweigh. If the weight is not constant repeat until it is. The increase in weight gives the amount of copper precipitated.

We have now (*a*) the weight of zinc used, (*b*) the weight of copper which this zinc has displaced. Calculate the weight of copper displaced by 32·5* grammes of zinc. This is given by

$$\frac{\text{Weight of copper displaced}}{\text{Weight of zinc used}} \times 32{\cdot}5.$$

If the experiment has been carried out accurately it will be found that 32·5 grammes of zinc replace 31·8 grammes of copper, and however many times the experiment is repeated the result will be the same.

We may say, therefore, that 32·5 grammes of zinc are *equivalent to* 31·8 grammes of copper

Next, let us investigate the composition of black copper oxide, in order to find out how many grammes of copper are equivalent to 8 grammes of oxygen.

Exp. 83.—Heat a crucible and lid: allow to cool, then weigh. Weigh out about 0·5 gramme of pure copper wire, and place in the crucible. Remove to a fume closet, then pour upon the metal one or two drops of water, followed by a *few* drops of strong nitric acid. If necessary, add more acid, to complete the solution of the wire. Gently evaporate down on a sand-bath, taking care that there is no loss by spirting. The green powder left is copper nitrate.

Support the crucible on a pipeclay triangle and heat till nothing but black copper oxide remains. Cool with the lid on, then weigh, and so find the weight of oxide.

Then the weight of copper which combines with 8 grammes of oxygen is given by

$$\frac{\text{Weight of copper}}{\text{Wt. of oxide} - \text{Wt. of copper}} \times 8.$$

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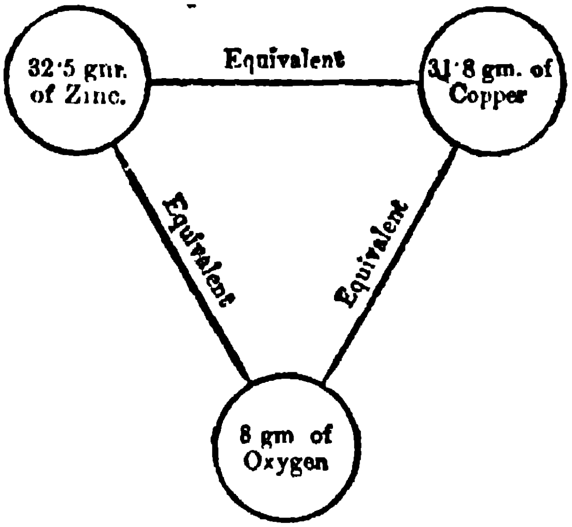
* We might, of course, calculate the weight of copper displaced by 1 gramme of zinc, and this seems the more natural course; the reason for choosing 32·5 grammes will be apparent later.

A good result will show that 31·8 grammes of copper unite with 8 grammes of oxygen to form black copper oxide, *i.e.* 31·8 grammes of copper are *equivalent to* 8 grammes of oxygen in this oxide.

Now, referring back to the previous results, we find that 31·8 grammes of copper and 8 grammes of oxygen are each equivalent to 32·5 grammes of zinc,* *i.e.* the weights of copper and zinc which are equivalent to a given weight of oxygen are also the weights of these metals which are equivalent to each other. Expressed diagrammatically, we have—



Now copper does not liberate hydrogen from dilute sulphuric or dilute hydrochloric acids as zinc does, so we cannot directly determine the weight of hydrogen displaced from an acid by this metal as we did in the case of zinc. This can, however, be done indirectly,† and it is found that 31·8 grammes of copper displace 1 gramme of hydrogen from sulphuric acid with formation of copper sulphate. In other words, 31·8 grammes of copper are *equivalent to* 1 gramme of hydrogen, and we may now construct the following diagram in which the two previous ones are combined:—

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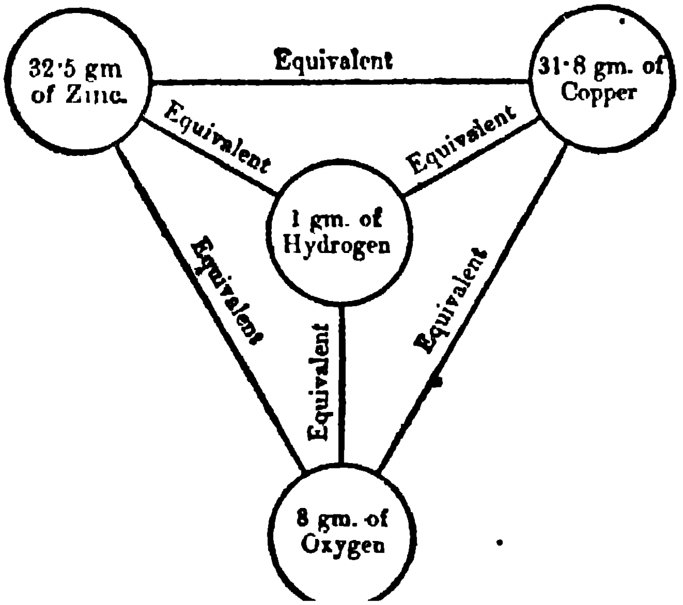
* It was in order to bring out this point that we calculated the weight of copper liberated by *32·5 grammes* of zinc in Exp. 82.

† *E.g.* by determining the weight of copper sulphate produced from a known weight of sulphuric acid by the action of black copper oxide.



56. **Law of Equivalents.**—The above results combined with those of a large number of experiments on similar lines have led to the conclusion that it is possible to assign to each element a number called its *chemical equivalent* (or *combining weight*) such that *the weights of elements which combine together are proportional to their chemical equivalents or to simple multiples of these.* The statement just given in italics is known as the *Law of Equivalents.*

The number chosen as the chemical equivalent of hydrogen is unity, and the *chemical equivalent*[*] (or *combining weight*) of an element may therefore be defined as *the weight of the element which combines with or displaces* 1 *gramme of hydrogen* (*or* 8 *grammes of oxygen,* which, as we have seen, are equivalent to 1 gramme of hydrogen).

A reference to the above diagram will show that the chemical equivalents of zinc and copper are respectively 32·5 and 31·8.

57. **Methods of determining Chemical Equivalents.**—

(1) *Determination of the weight of the element which combines with* 1 *gramme of hydrogen.*

[*] Also called the *equivalent weight,* or simply the *equivalent.*

This gives the chemical equivalent in terms of hydrogen directly, but it is not a method of general application. It has been used in determining the equivalent of oxygen, and this may be deduced from the results of Exp. 67.

(2) *Determination of the volume of hydrogen evolved by the action of a metal on an acid.*

Here again the value of the equivalent is found directly in terms of hydrogen; it is given by

$$\frac{\text{Weight of Metal used}}{\text{Weight of hydrogen evolved}}.$$

The method of experiment was illustrated in Exp. 81, using zinc.

This method may also be employed in the case of a few other metals, *e.g.* magnesium, iron, and aluminium.

In the case of the last metal, dilute *hydrochloric* acid must be used in place of dilute sulphuric acid, which only acts very slowly on the metal.

(3) *Determination by displacement of one metal by another.*

This is an indirect method which can be applied in some cases where Method 2 is not available.

Suppose a metal, A, whose equivalent is known displaces from its salts a metal, B, whose equivalent is to be determined. Then if x grammes of A displace y grammes of B we have

$$\frac{\text{Equivalent of B}}{\text{Equivalent of A}} = \frac{y}{x},$$

from which the equivalent of B can be calculated.

The method of carrying out the experiment is that adopted in Exp. 82, in which zinc displaces copper from copper sulphate. In place of zinc the metal iron might have been used. The equivalent of silver may be similarly determined by using a solution of silver nitrate instead of copper sulphate, and any one of the three metals zinc, iron, and magnesium.

(4) *Conversion into the oxide.*—In many cases the most convenient method of finding the equivalent of a metal

consists in converting a weighed quantity of it into its oxide, and weighing the oxide produced. From the results obtained we calculate the weight of the metal which combines with 8 grammes of oxygen.

Sometimes, as in the case of magnesium, the metal is readily converted into its oxide by heating in air. (Exp. 65 (*a*)).

Usually, however, the direct oxidation of a metal by heating in air is a slow and imperfect process, and it is best to first convert the metal into the nitrate and then break this up by ignition, when a residue of the oxide remains. We adopted the latter method in the case of copper in Exp. 83. The equivalents of lead and tin may be determined in a similar way; in the latter case nitric acid converts the metal directly into the oxide.

(5) *Conversion of the oxide into the metal.*—The converse of Method 4 may also be conveniently applied in some cases, namely, the reduction of a weighed quantity of the oxide of a metal to the metal, the weight of which is then ascertained. The reduction may be brought about by heating the oxide in a current of hydrogen, coal gas, or carbon monoxide. Suitable oxides to experiment with would be cupric oxide and litharge, the experiment being conducted on the lines of Exp. 68.

(6) *Determination of the composition of the chloride.*—The great majority of the elements form compounds with the non-metal chlorine. Now it has been found that 35·5 grammes of chlorine unite with 1 gramme of hydrogen to form hydrogen chloride, *i.e.* the equivalent of chlorine is 35·5. If, therefore, we find the weight of an element which unites with 35·5 grammes of chlorine, this weight is the equivalent of the element.

One method of determining the composition of the chloride of a metal consists in heating a weighed quantity of the metal in a current of chlorine and weighing the chloride formed. This method was employed by Stas in the case of silver.

The methods of determining equivalents referred to above are of course by no means exhaustive; a large number of others have been applied in particular cases.

Elements may have more than one equivalent.—

From a consideration of the Law of Multiple Proportion it is obvious that some elements at any rate may have more than one equivalent. For example, the equivalent of lead in the puce oxide is different from its equivalent in litharge. We can deduce the two values from the results of Exp. 68, in which we found that

6·45 grammes of lead unite with 1 gramme of oxygen to form puce oxide of lead.

12·9 grammes of lead unite with 1 gramme of oxygen to form litharge.

It follows that

6·45 × 8 or 51·6 grammes of lead unite with 8 grammes of oxygen to form puce oxide of lead,

and

12·9 × 8 or 103·2 grammes of lead unite with 8 grammes of oxygen to form litharge,

i.e. the equivalents of lead in the puce oxide and in litharge are respectively 51·6 and 103·2.

Again, the weights of carbon which combine with 8 grammes of oxygen to form carbon monoxide and carbon dioxide respectively are 6 and 3 grammes; *i.e.* the equivalent of carbon in the monoxide is 8, and in the dioxide 4.

In all cases, however, where an element has more than one equivalent the different equivalents bear a simple numerical relation to each other; this follows from the Law of Multiple Proportion. In the cases considered above, for example, the equivalents of lead and carbon are respectively in the simple ratios 51·6 : 103·2 = 1 : 2 and 8 : 4 = 2 : 1.

58. **Equivalents of Compounds.**—The term *equivalent* is also used with reference to *compounds.* Consider, for example, the action of *acids* and *bases.* It is found that 36·5 grammes of hydrochloric acid and 49 grammes of sulphuric acid respectively neutralise 40 grammes of caustic soda, and that the same weights of these acids respectively neutralise 56 grammes of caustic potash. We may say therefore that 36·5 grammes of hydrochloric acid,

49 grammes of sulphuric acid, 40 grammes of caustic soda, and 56 grammes of caustic potash are *equivalent quantities* of these substances.

The *equivalent* of an *acid* is defined as *the weight of the acid which contains* 1 *gramme of hydrogen replaceable by a metal*, and the *equivalent* of a *base* as *the weight of it which neutralises the equivalent of an acid.* 36·5 grammes of hydrochloric and 49 grammes of sulphuric acid each contain 1 gramme of hydrogen replaceable by a metal, so the equivalents of these acids are respectively 36·5 and 49; also the equivalents of caustic soda and caustic potash are 40 and 56 respectively, since these are the weights which neutralise the equivalent of an acid.

Further, we may define the equivalent of a *salt* as the weight of it produced by neutralising the equivalent weight of an acid by a base. Thus the weight of sodium chloride formed when 36·5 grammes of hydrochloric acid are neutralised by caustic soda is 58·5 grammes, the equivalent of sodium chloride is therefore 58·5.

59. **Dalton's Atomic Theory.**—Over a century ago Dalton propounded the theory that there is a limit to the masses of the ultimate particles of matter capable of taking part in chemical change; that, for instance, when oxygen is attached to an element or transferred from one element to another, the amount so transferred is not indefinitely or infinitely small, but that the transfer takes place *step by step* in masses of definite dimensions. These ultimate particles he regarded as being incapable of further division, and hence termed them *atoms.*[*] His theory is thus known as the *Atomic Theory.*

This theory affords a satisfactory explanation of both the *Law of Multiple Proportions* (first established by Dalton) and the *Law of Equivalents,* and these Laws form the foundation on which the theory mainly rests.

It is important that the student should realise that atoms are excessively small, and we can never hope to see them even with microscopes many times more powerful than the best that are in use at the present time.

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[*] From the Greek ἀ, not; τέμνω, I cut.

Small as the atoms are, their *relative weights* have been determined, and some of these will be found in the table in § 86, hydrogen being taken as unity. Further, very approximate determinations of the *absolute* weight of atoms have recently been made.

60. **Gay-Lussac's Law.**—Experiments have been described in § 32 which show that the volumes of hydrogen and oxygen which combine to form water are in the ratio 2 : 1.

If we modify the synthetic experiment (Exp. 48) in such a way that the water produced remains in the form of steam (by surrounding the eudiometer with a jacket filled with the vapour of a liquid boiling at a temperature considerably above 100° C., the boiling-point of water), we find that the volume of steam produced is equal to that of the hydrogen it contains. (The gases before combination are of course measured at the same temperature as the steam.)

There is then a *simple relation* between the volumes of hydrogen and oxygen which combine together and the volume of steam they produce.

Experiments with other substances have been found to yield similar results (as we shall see in the sequel). For example:—

1 vol. of hydrogen and 1 vol. of chlorine combine to form 2 vol. of hydrochloric acid gas.
2 vol. of carbon monoxide and 1 vol. of oxygen combine to form 2 vol. of carbon dioxide.
1 vol. of nitrogen and 3 vol. of hydrogen combine to form 2 vol. of ammonia.
2 vol. of nitric oxide and 1 vol. of oxygen unite to form 2 vol. of nitrogen peroxide.

Gay-Lussac performed a number of experiments like those referred to, at the beginning of the last century, and generalised the results in the following statement, known as *Gay-Lussac's Law of Volumes*:—

When gases combine together they do so in volumes which bear a simple ratio to one another and to that of the product (if a gas).

61. Avogadro's Hypothesis.—Gay-Lussac announced the Law of Volumes a short time after Dalton had put forward his Atomic Theory, and an attempt was soon made to harmonise the two. To this end the hypothesis that *equal volumes of all gases contain the same number of atoms* was advanced.*

It was soon found, however, that this hypothesis was untenable. The following example will illustrate the kind of argument which led to this conclusion.

Consider the combination of hydrogen and chlorine to form hydrochloric acid gas. *One* volume of hydrogen combines with one volume of chlorine to form *two* volumes of hydrochloric acid gas. Let $x =$ number of atoms† of hydrochloric acid gas in *two* volumes; then by the hypothesis *one* volume of hydrogen will contain $x/2$ atoms of hydrogen and *one* volume of chlorine $x/2$ atoms of chlorine. Now let us take as two volumes such a volume that $x = 1$ (since we can, of course, take any volume we like). Then $x/2 = \frac{1}{2}$. In other words, one atom of hydrochloric acid gas (contained in two volumes) is produced by the union of half an atom of hydrogen (contained in one volume) and half an atom of chlorine (contained in one volume). But, according to Dalton's theory, an atom cannot be divided; hence the hypothesis is incorrect.

The problem was solved by the Italian physicist Avogadro, who recognised two kinds of ultimate particles—

(*a*) The ultimate particle which can exist in the free state, as, for instance, the smallest particle of hydrochloric acid gas or of hydrogen. This he termed the *molecule.*

(*b*) The ultimate particle which is capable of taking part in a chemical change or capable of being transferred from one chemical compound to another, as, for instance, the hydrogen or the chlorine contained in the molecule of hydrochloric acid gas. This he termed the *atom.*

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* It should be noted that the term "atom" was used loosely here, because both elementary and compound gases were included, and it is obviously a contradiction in terms to speak of an *atom* of a *compound,* since a compound can be broken up into elements. By an "atom" of a compound was meant the smallest particle of the compound which can exist.

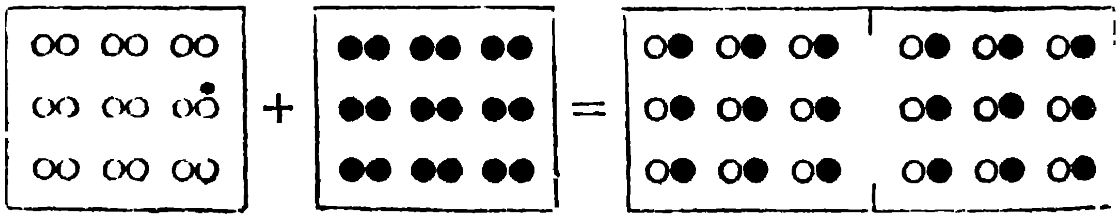
† Atom being used here in the loose sense already explained.

A molecule of a compound must necessarily contain at least two atoms. A molecule of an element may contain two or more atoms, or it may consist of one atom only.

Avogadro then restated the hypothesis which had been shown to be untenable, as follows:—*Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.*

Let us return to the above example, namely, the combination of hydrogen and chlorine to form hydrochloric acid gas, and reconsider it in the light of Avogadro's hypothesis. We will make the assumption that the molecules of hydrogen and chlorine are each composed of two atoms,[*] and that a molecule of hydrochloric acid gas is composed of one atom of hydrogen and one atom of chlorine. Further, we will consider the combination of *nine* molecules of each gas (any other number would do equally well). Then, assuming Avogadro's hypothesis, the combination may be represented as below, where

○ represents an atom of hydrogen.
○○ ,, a molecule of ,,
● ,, an atom of chlorine.
●● ,, a molecule of ,,



Nine molecules
or
1 volume.

Nine molecules
or
1 volume.

Eighteen molecules
or
2 volumes.

But this agrees with the results of experiment: *i.e.* Avogadro's hypothesis harmonises Gay-Lussac's Law and Dalton's Atomic Theory as far as the combination of hydrogen and chlorine is concerned. By means of similar diagrams it can be shown that the hypothesis affords a satisfactory explanation of the volumetric relations of the other gases considered in this chapter; in fact its applicability has been found to be perfectly general, and we may consider that its truth is thoroughly well established.

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[*] There are very good grounds for this assumption, but we cannot stop to consider them here.

62. **Symbols and Formulae.**—In order to represent an *atom* of an element we use a *symbol* which is an abbreviation of the name of the element. In many cases the initial letter of the name of an element is used as the symbol: *e.g.* an atom of hydrogen is represented by H and an atom of oxygen by O. When the names of two or more elements commence with the same letter, two significant letters are used—the first and one other; one of the elements may, however, be represented by the initial letter only. For example, the names of four elements commence with B—barium, bismuth, boron, and bromine; the symbols for the atoms of these elements are Ba, Bi, B, and Br respectively. Some chemical symbols are derived from the Latin names of the elements they represent; thus an atom of copper is represented by Cu (Lat., *cuprum*) and an atom of iron by Fe (Lat., *ferrum*).

Now the weights of the elements represented by the symbols for their atoms will of course be the weights of the atoms. These are expressed in terms of the weight of an atom of hydrogen as unity, so that the symbols H and O stand for unit weight of hydrogen and 16 units of weight of oxygen respectively (the atomic weight of oxygen being 16).

When the number of atoms in a molecule of an element is known, the *molecule* is represented by placing a small number below and to the right of the symbol for the element. For example, a molecule of oxygen is represented by O_2, since the molecule of oxygen contains two atoms; O_2 further represents 2×16 or 32 units of weight of oxygen.

If the molecule of the element only contains *one* atom, the suffix is omitted, *e.g.* the molecule of mercury is represented by Hg.

When we wish to represent the composition of compounds we use *formulae*.* The formula for a molecule of a compound is built up by placing the symbols for the atoms of the elements of which it is composed in juxtaposition, and adding suffixes to indicate the number of atoms of each element present. A molecule of water, for example, is represented by the formula H_2O, which implies that two atoms of hydrogen or two units of weight are combined with one atom of oxygen or 16 units of weight, to form one molecule of water weighing 18 units (*i.e.* the *molecular weight* of water is 18 units).

When we do not know the *absolute* number of atoms of each element in a molecule of the compound, as is usually the case when the substance is not in the gaseous state, we write the simplest possible formula which represents the *relative* number of atoms of each element. Thus the number of atoms of copper and oxygen contained in a molecule of black oxide of copper is unknown, but we do know that for every atom of copper there is one of oxygen, so we write the formula for the oxide CuO.

63. **Equations.**—A *chemical equation* is an equation which represents the nature and relative amounts of the bodies concerned in a chemical change by means of symbols.

Certain chemical substances being brought together under suitable conditions, a chemical change takes place by which one or more of the constituents is set free or transferred, the state before and after the change being separated by the sign $=$.

As instances of such equations we may give the action of hydrogen at red heat on black oxide of copper—

$$\underset{\text{Hydrogen}}{H_2} + \underset{\substack{\text{Black oxide}\\\text{of copper}}}{CuO} = \underset{\text{Water}}{H_2O} + \underset{\text{Copper}}{Cu}$$

and the action of zinc on dilute sulphuric acid—

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}.$$

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* The term *formula* is also frequently applied to the symbol for a *molecule* of an *element*.

Such equations may be interpreted quantitatively according to the table of atomic weights given in § 64. Thus—

2 × 1 or 2 units of weight of hydrogen will effect the reduction of 63·5 + 16 or 79·5 units of weight of black oxide of copper, yielding 2 × 1 + 16 or 18 units of weight of water and 63·5 units of weight of copper.

In the second case

65·5 units of weight of zinc acting upon 2 × 1 + 32 + 4 × 16 or 98 units of weight of sulphuric acid yield 65·5 + 32 + 4 × 16 or 161·5 units of weight of zinc sulphate and 2 units of weight of hydrogen

It is obvious, from a consideration of the Law of Conservation of Matter, that the quantity of each element and the total quantity of the elements on each side of the equation must be the same. Thus in the first equation discussed above there are on each side two atoms of hydrogen or 2 units of weight, one atom of copper or 63·5 units of weight, and one atom of oxygen or 16 units of weight. The total weight of the elements on each side of the equation is 2 + 63·5 + 16 or 81·5 units.

In writing equations to express chemical reactions, regard must be paid to the state in which the bodies concerned exist. If in the *solid* condition (and often also if in the *liquid* condition), the molecular composition of a substance is usually undefined, and a mere empirical statement of the quantity of the substance entering into the reaction must be made. If in the *gaseous* condition, the molecular composition is known and must be indicated.

$2S$ and S_2 both represent 64 units of weight of sulphur. The first is the form used for expressing a certain weight of solid sulphur; the second expresses the same weight of sulphur in the form of vapour at a high temperature, it being known that the molecule of sulphur at high temperature is composed of two atoms.

Again, the equation

$$H_2 + O = H_2O,$$

though it indicates that hydrogen and oxygen unite to form water in the proportion of 2 × 1 units of weight of hydrogen to 16 units of weight of oxygen (which agrees with the result of Exp. 67), is not a correct representation of the combination of these gases; for O represents an atom of oxygen which cannot exist in the free state, but immediately unites with another atom to form a molecule. The equation must therefore be doubled thus—

$$2H_2 + O_2 = 2H_2O.$$

It will be noticed that in doubling the equation we have written $2H_2$, not H_4; this is because the molecule of hydrogen contains 2, not 4, atoms. $2H_2$ represents two molecules of hydrogen each composed of two atoms; H_4 would represent one molecule containing 4 atoms.

Avogadro's hypothesis enables us to give a volumetric meaning to equations when they represent the interaction of gases, for since equal volumes of all gases contain the same number of molecules, it follows that the volume occupied by one molecule* of any gas (elementary or compound) is the same. It is usual, for the sake of convenience, to arbitrarily fix the volume of one molecule of a gas as *two volumes*.

Consider again the last equation given above. It may be read thus:—2 molecules or 4 volumes of hydrogen unite with 1 molecule or 2 volumes of oxygen to form 2 molecules or 4 volumes of steam; *i.e.* hydrogen unites with half its volume of oxygen to form its own volume of steam, which agrees with the result of experiment.

Again, the equation

$$H_2 + Cl_2 = 2HCl,$$

which represents the combination of hydrogen and chlorine, may be interpreted thus:—1 molecule or 2 volumes of hydrogen combines with 1 molecule or 2 volumes of chlorine to form 2 molecules or 4 volumes of hydrogen chloride; *i.e.* hydrogen chloride contains half its volume of hydrogen and half its volume of chlorine, which agrees with the results of experiment.

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* By the expression "volume occupied by one molecule" we mean the volume occupied by the molecule and also its share of the free space between the molecules.

Below are given the equations for a few of the reactions we investigated in Chapter VII. and their quantitative interpretations. You will find that these are in agreement with the results of the experiments.

Formation of Magnesium Oxide.—

$$2Mg + O_2 = 2MgO,$$

$2Mg$	O_2	$2MgO$
2 × 24·5 or 49 units of weight of magnesium	2 × 16 or 32 units of weight of oxygen	2 × (24·5 + 16) or 81 units of weight of magnesium oxide

i.e. 1 gram of magnesium combines with 32/49 or 0·65 gram of oxygen. Compare this with Exps. 65(*a*), 65(*b*).

Decomposition of Chalk.—

$$CaCO_3 = CaO + CO_2.$$

$CaCO_3$	CaO	CO_2
40 + 12 + 3 × 16 or 100 units of weight of calcium carbonate (chalk)	40 + 16 or 56 units of weight of calcium oxide (lime)	12 + 2 × 16 or 44 units of weight of carbon dioxide

Compare this with Exp. 66.

Reduction of the Oxides of Lead by Hydrogen.—

$$PbO_2 + 2H_2 = Pb + 2H_2O,$$

PbO_2	$2H_2$	Pb	$2H_2O$
Lead peroxide 207 + 2 × 16 or 239 units of weight	Hydrogen 2 × 2 or 4 units of weight	Lead 207 units of weight	Water 2(2 × 1 + 16) or 36 units of weight

$$PbO + H_2 = Pb + H_2O.$$

PbO	H_2	Pb	H_2O
Yellow oxide of lead 207 + 16 or 223 units of weight	Hydrogen 2 × 1 or 2 units of weight	Lead 207 units of weight	Water 2 × 1 + 16 or 18 units of weight

Compare these numbers with the results obtained in Exp. 68.

Action of Heat on Copper Sulphate Crystals.—Copper sulphate crystals are represented by the formula $CuSO_4, 5H_2O$, which means that a molecule of copper sulphate, $CuSO_4$, is loosely combined with 5 molecules of water of crystallisation. The equations representing the decomposition of the crystals are as follows:—

At 140° C., $CuSO_4, 5H_2O = CuSO_4, H_2O + 4H_2O$.

At 220° C., $CuSO_4, H_2O = CuSO_4 + H_2O$.

These equations agree with the results of Exp. 69, for they represent that four-fifths of the water of crystallisation (four molecules out of five) is given up at 140°, the remaining fifth being driven off only at 220° C.

64. **The chief Elements,** the symbols representing them, and their atomic weights (in round numbers) in relation to hydrogen as unity are given in the table below. Non-metals are printed in italics.

Aluminium	Al	27
Antimony	Sb	120
Argon	A	40
Arsenic	As	75
Barium	Ba	137
Bismuth	Bi	208
Boron	B	11
Bromine	Br	80
Cadmium	Cd	112
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35·5
Chromium	Cr	52
Cobalt	Co	59
Copper	Cu	63·5
Fluorine	F	19
Gold	Au	197
Helium	He	4
Hydrogen	H	1·0
Iodine	I	127
Iron	Fe	56
Lead	Pb	207
Lithium	Li	7
Magnesium	Mg	24·5
Manganese	Mn	55
Mercury	Hg	200
Molybdenum	Mo	96
Nickel	Ni	59
Nitrogen	N	14
Oxygen	O	16
Phosphorus	P	31
Platinum	Pt	195
Potassium	K	39
Silicon	Si	28·5
Silver	Ag	108
Sodium	Na	23
Strontium	Sr	87·5
Sulphur	S	32
Tin	Sn	119
Titanium	Ti	48
Zinc	Zn	65

65. **Valency.**—The best way to approach the subject of valency is to consider the composition of a number of stable compounds of hydrogen and another element. The formulae of ten such compounds are given below—

HF, Hydrogen fluoride.
HCl, Hydrogen chloride.
HBr, Hydrogen bromide
HI, Hydrogen iodide.
H_2O, Water.
H_2S, Sulphuretted hydrogen.
H_3N, Ammonia.
H_3P, Phosphoretted hydrogen.
H_4C, Marsh gas.
H_4Si, Silicon hydride.

We cannot study the metals in a similar manner so satisfactorily because many of them do not form stable compounds with hydrogen. Let us instead compare the formulae of a series of compounds (salts) derived from some acid, say hydrochloric acid (HCl), by the replacement of the hydrogen by metals. We have—

(1) $NaCl$, KCl.

(2) $CuCl_2$, $MgCl_2$, $CaCl_2$, $ZnCl_2$, $BaCl_2$.

(3) $AlCl_3$, $FeCl_3$, $CrCl_3$.

The compounds in Group (1) are obviously derived from one molecule of hydrochloric acid, those in Group (2) from two molecules, and those in Group (3) from three molecules, because they contain respectively one, two, and three atoms of chlorine. It follows that—

(1) One atom of sodium or potassium replaces *one atom* of hydrogen.

(2) One atom of copper, magnesium, etc., replaces *two atoms* of hydrogen.

(3) One atom of aluminium, iron, or chromium replaces *three atoms* of hydrogen.

In other words, one atom of sodium or potassium possesses the same power of combining with the non-metal chlorine as one atom of hydrogen; one atom of copper, magnesium, etc., has the same combining capacity as two atoms of hydrogen; and one atom of aluminium, iron, or chromium as three atoms of hydrogen.

An examination of the compounds derived in a similar manner from other acids, *e.g.* sulphuric, nitric, and phosphoric acids, leads to like conclusions; we find, for instance, that one atom of sodium replaces one atom of hydrogen, and one atom of aluminium replaces three atoms of hydrogen, whichever acid is used.

Taking the atom of hydrogen as the standard, and calling its capacity to combine with other elements, or its *valency* (*i.e.* worth), unity, a number can be assigned to each element which expresses its combining capacity or valency in terms of this unit. Thus, since one atom of chlorine unites with *one* atom of hydrogen, the valency of chlorine is the same as that of hydrogen, viz. 1. One atom of oxygen unites with *two* atoms of hydrogen; consequently the valency of oxygen is 2. Similarly the valencies of nitrogen and carbon are 3 and 4 respectively. Again, one atom of sodium or of potassium possesses the same combining capacity as one atom of hydrogen; sodium and potassium have, therefore, a valency 1. Similarly the valency of copper, magnesium, etc., is 2, and of aluminium, etc., 3.

An element with a valency 1 is said to be *monovalent*, and the corresponding terms *divalent*, *trivalent*, etc., are applied to elements whose valencies are respectively 2, 3, etc. Thus hydrogen, chlorine, and potassium are monovalent, oxygen and copper are divalent, nitrogen and aluminium are trivalent, and carbon is tetravalent.

It must be added that certain metals, such as iron and tin, form two series of salts in which they show different valency. For instance, in $FeCl_2$ (ferrous chloride) one atom of iron replaces *two* atoms of hydrogen, *i.e.* iron is *divalent*, whilst in $FeCl_3$ (ferric chloride) one atom of iron replaces *three* atoms of hydrogen, *i.e.* iron is *trivalent*; in the same way we have *stannous* and *stannic* chlorides ($SnCl_2$ and $SnCl_4$) in which the valency of tin is *two* and *four* respectively.

The valencies of the majority of the elements, both metals and non-metals, can be found from a study of their *oxides* if we assume that oxygen is divalent. Let us examine the formulae of a number of oxides—

Na_2O, K_2O, Cl_2O.
CuO, MgO, CaO, ZnO, BaO, PbO, FeO.
Al_2O_3, B_2O_3.
CO_2, SO_2, SiO_2.
N_2O_5, I_2O_5.
SO_3.

We conclude that in these compounds Na, K, Cl are monovalent; Cu, Mg, Ca, etc., are divalent; Al, B are trivalent; C, S (in SO_2), and Si are tetravalent; N (in N_2O_5), P (in P_2O_5), I (in I_2O_5) are pentavalent; S (in SO_3) is hexavalent.

It will be observed that several of the non-metals, *e.g.* iodine, nitrogen, and sulphur, are capable of exerting a higher valency towards oxygen than towards hydrogen; thus iodine is *monovalent* in HI and *pentavalent* in I_2O_5, nitrogen is *trivalent* in NH_3 and *pentavalent* in N_2O_5, sulphur is *divalent* in H_2S and *tetravalent* and *hexavalent* in SO_2 and SO_3 respectively. In general an element which is hexavalent may, in some of its compounds, be tetravalent or divalent, and one which is pentavalent may be trivalent. It should be mentioned, however, that many elements exhibit both an odd and an even valency, contrary to the belief of the earlier chemists.

The valencies of a number of common elements are given in the following table:—

Monovalent.	Divalent.	Trivalent.	Tetravalent.	Pentavalent.	Hexavalent.
H	Ba	Al	Sn (ic)	P (in PCl_5, etc.)	S (in SO_3, etc.)
Na	Sr	Cr	C	N (in N_2O_5, etc.)	Cr (in CrO_3).
K	Ca	Fe (ic)	Si	As (ic)	
Ag	Mg	Co (ic)	S (in SO_2, etc.)	Sb (ic)	
F	Zn	As (ous)	Pb (in PbO_2, etc.)		
Cl	Cd	Sb (ous)			
Br	Co	Bi			
I	Ni	B			
	Pb	P (in PCl_3, etc.)			
	Hg	N (in NH_3, etc.)			
	Cu				
	Fe (ous)				
	Mn (ous)				
	Sn (ous)				
	O				
	S (in H_2S, etc.)				

66. Nomenclature of Compounds.—Compounds may be divided into two classes, those composed of *two elements* (called "binary" compounds), and those composed of *three or more elements.*

Binary compounds may be designated according to the number of atoms of the elements they contain, the number being usually stated only for the more non-metallic element, the termination of the name being *-ide*—

H_2O_2, hydrogen diox*ide*.
I_2O_5, iodine pentox*ide*.
PCl_3, phosphorus trichlor*ide*.
PCl_5, phosphorus pentachlor*ide*.

Where only two compounds of the same elements exist, the termination *-ous* may be applied to the one with the smaller proportion of the more non-metallic element (the "lower" oxide, iodide, etc.), and the termination *-ic* to the other—

HgI, mercur*ous* iodide; HgI_2, mercur*ic* iodide.
Cu_2O, cupr*ous* oxide; CuO, cupr*ic* oxide.

Oxides which when dissolved in water form acids are termed "anhydrides," and these, together with the acids they give rise to, receive the terminations *ous* and *ic* in the same sense as before—

N_2O_3, nitr*ous* anhydride or nitrogen trioxide; HNO_2, nitr*ous* acid.

N_2O_5, nitr*ic* anhydride or nitrogen pentoxide; HNO_3, nitr*ic* acid.

CO_2, carbon*ic* anhydride or carbon dioxide; H_2CO_3, carbon*ic* acid.

Salts take the termination *ite* or *ate* according as they are derived from *ous* or *ic* acids respectively—

H_2SO_3, sulphur*ous* acid;	Na_2SO_3, sodium sulph*ite*.
H_2SO_4, sulphur*ic* acid;	Na_2SO_4, sodium sulph*ate*.
HNO_2, nitr*ous* acid;	$NaNO_2$, sodium nitr*ite*.
HNO_3, nitr*ic* acid;	$NaNO_3$, sodium nitr*ate*.

Where more than two compounds of the same element exist further discrimination is necessary, and in the case of acids and salts the prefix *hypo* is applied to the lowest and *per* to the highest.

$HClO$, *hypo*chlorous acid;	$KClO$, potassium *hypo*chlor*ite*.
$HClO_2$, chlor*ous* acid;	$KClO_2$, potassium chlor*ite*.
$HClO_3$, chlor*ic* acid;	$KClO_3$, potassium chlor*ate*.
$HClO_4$, *per*chloric acid;	$KClO_4$, potassium *per*chlor*ate*.

QUESTIONS.—CHAPTERS VIII. AND IX.

1. Enunciate Boyle's Law. Describe an experiment which illustrates it.
2. How would you proceed to find the density of carbon dioxide?
3. Describe how you would proceed to measure the volume of hydrogen evolved from half a gramme of magnesium by the action of sulphuric acid.
4. How would you proceed to estimate (1) the mass, (2) the volume of oxygen evolved on heating 1 gramme of red lead till decomposition was complete?
5. Describe experiments to illustrate the phenomenon of *diffusion of gases.*
6. What do you understand by the *chemical equivalent* of an element? Describe an experiment by which the equivalent of magnesium can be determined.
7. Describe in detail how you would proceed to find the chemical equivalent of copper by deposition of the metal, assuming the equivalent of zinc known.
8. How would you proceed to determine the equivalent of aluminium, given a supply of the metal, some strong hydrochloric acid and some water?
9. State *Gay-Lussac's Law of Combination of Gases by Volume,* and illustrate it by examples.
10. Explain *fully* what the formulae O_2 and CO_2 represent.
11. State all that is implied by the chemical equation

$$2H_2 + O_2 = 2H_2O.$$

12. What is Avogadro's hypothesis? Indicate the nature of the evidence on which it is based.
13. Explain the term *valency,* illustrating your answer by examples.
14. Give examples of elements which exhibit more than one valency, and illustrate the way in which the composition of their compounds changes with the change in valency.
15. Explain the term *binary compound,* and give three examples of binary compounds.

SECTION II.—SYSTEMATIC TREATMENT OF THE NON-METALS.

CHAPTER X.

HYDROGEN, H_2.

67. **Occurrence.**—Hydrogen occurs in the free state as an incandescent gas in the sun, but in the earth it is always found in combination with other elements. Water is a compound of hydrogen and oxygen, H_2O; many oils consist of hydrogen and carbon, and these elements, together with oxygen, form the chief constituents of animal and vegetable tissue, and of organic compounds in general.

68. **Methods of Preparation.**—The more important of these have already been described in Chapter IV. and only require brief recapitulation here; some other methods will, however, also be mentioned.

(1) **Direct decomposition of water by heat.**—On heating water to a high temperature, it undergoes partial decomposition. Grove effected this by passing steam through a strongly heated porcelain tube.

(2) **Decomposition of water by the electric current.**—This process is described in Exp. 47.

(3) **Decomposition of water by metals at ordinary temperature.**—Refer back to § 27 for an experiment illustrating this method of obtaining hydrogen. The metals which will decompose water without the application of heat are comparatively few in number; they comprise the alkali metals (sodium, potassium, lithium, etc.), the metals of the alkaline earths (calcium, strontium, barium), and magnesium (very slowly). Only half the hydrogen is liberated,

the equation representing the reaction in the case of sodium being—

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Caustic soda.}}{2NaOH} + \underset{\text{Hydrogen}}{H_2}.$$

Caustic soda ($NaOH$) is formed and dissolves in the water, rendering it alkaline, as may be shown by pouring red litmus solution into the liquid.

Some metals which by themselves cannot decompose water at ordinary temperatures are able to do so when in contact with certain other metals. Thus if zinc be coated with a thin layer of copper—forming a so-called *zinc-copper-couple**—it slowly liberates hydrogen from the water in which it is immersed without the application of heat. On warming, hydrogen is rapidly evolved; this provides a convenient method of preparing the pure gas. The zinc alone takes part in the reaction; it is converted into zinc hydroxide, $Zn(OH)_2$—

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

Again, the metals zinc and magnesium will decompose water readily at ordinary temperature if they are in contact with platinum. A discussion of the explanation of these contact decompositions is beyond the scope of this work.

(4) **Decomposition of water by metals on the application of heat.**—This method of preparing hydrogen was studied in Exp. 37.

When heated metals decompose steam they displace the whole of the hydrogen, and are converted into oxides—

$$3Fe + 4H_2O = \underset{\text{Magnetic oxide of iron.}}{Fe_3O_4} + 4H_2.$$

$$Mg + H_2O = \underset{\text{Magnesium oxide of magnesia.}}{MgO} + H_2.$$

Most metals will decompose water provided the temperature is sufficiently high; copper, silver, and gold are notable exceptions.

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* The *zinc-copper-couple* is prepared by immersing granulated zinc in a dilute solution of copper sulphate for a short time, and then removing the product and washing it well with water to remove adhering salts.

(5) **Action of acids on metals.**—Many metals act on dilute hydrochloric acid or dilute sulphuric acid with evolution of hydrogen. The common laboratory method of preparing the gas is to act on granulated zinc with dilute sulphuric acid, as described in Exp. 41.

The equation representing the reaction is—

$$\underset{\text{}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

(6) **Action of alkalis on metals.**—A few metals, notably zinc and aluminium, are acted upon by a boiling solution of caustic potash (KOH) or caustic soda (NaOH) with liberation of hydrogen. If zinc and caustic potash are used, the reaction which takes place is represented by the equation—

$$Zn + 2KOH = \underset{\text{Potassium zincate.*}}{Zn(OK)_2} + H_2.$$

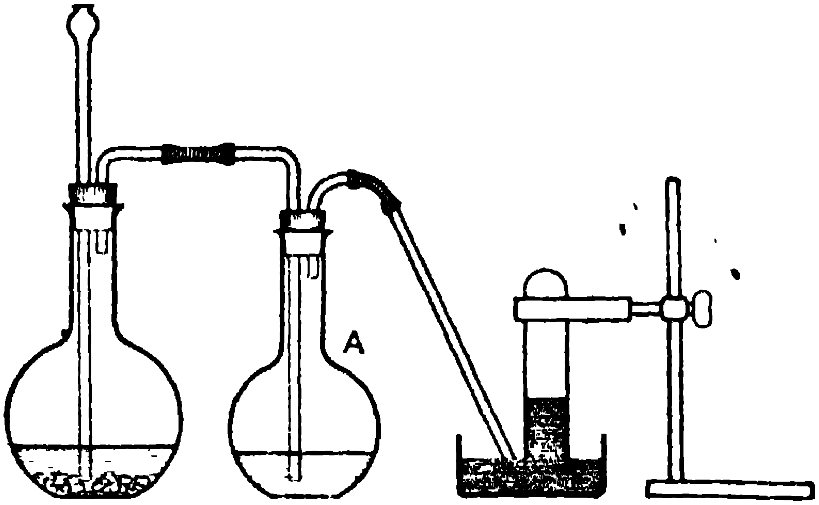

Fig. 27.

69. **Preparation of Pure Dry Hydrogen.**—The gas obtained by the common laboratory method (Method 5) is by no means pure. The best laboratory method for the preparation of pure hydrogen consists in acting on *magne-*

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* This compound is considered to exist in the residual solution, though it has not actually been isolated.

sium with dilute sulphuric acid. If the gas is required dry it should be passed through a small flask containing strong sulphuric acid* (A, Fig. 27) and collected at the pneumatic trough over mercury (water obviously being inadmissible).

70. Properties.—Hydrogen is a colourless, odourless gas, only very slightly soluble in water, 1 c.c. of which dissolves about 0·02 c.c. of the gas at ordinary temperatures. It is the lightest substance known, its *absolute density*, i.e. the weight of one cubic centimetre of it under standard conditions of temperature and pressure being only 0·00009 gram. The density of air under the same conditions is about 14·4 times that of hydrogen. The lightness of hydrogen as compared with air may be shown by suspending a beaker upside down from a balance and counterpoising; hydrogen is then poured upwards into it so as to displace the air, when the beaker will show a decrease of weight.

Hydrogen burns in air or oxygen with a blue non-luminous flame, which is very hot A solid infusible substance placed in the flame becomes white hot, and emits a brilliant light. This is the principle of the *lime-light,* in which a jet of hydrogen (or coal-gas) burning in oxygen impinges on a cylinder of quicklime and raises it to a white heat.

In burning, hydrogen combines with oxygen, forming water—

$$2H_2 + O_2 = 2H_2O.$$

A mixture of hydrogen with oxygen or air is violently explosive, as the combustion is practically instantaneous. Hence care has to be taken in experiments with hydrogen not to apply a light to the gas or to heat any part of the apparatus till the air has been expelled.

Hydrogen will not support the combustion of those substances which burn in air. Thus a lighted taper is extinguished on being pushed up into an inverted gas-jar of hydrogen; the gas of course takes fire and burns at the mouth of the jar.

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* The drying is rendered more complete by the use of two sulphuric acid flasks.

71. **Hydrides.**—Hydrogen forms compounds with most of the non-metals (either directly or indirectly) and with many of the metals; these compounds are called ***hydrides.*** The hydrides of the non-metals are, as a whole, stable compounds, but those of the metals are unstable. Examples of non-metallic hydrides are hydrogen chloride, HCl, water, H_2O, ammonia, NH_3, and marsh gas, CH_4; examples of hydrides of the metals are potassium hydride, KH, sodium hydride, NaH, and copper hydride, Cu_2H_2.

72. **Reducing Agents.**—We have seen in Exp. 44 that hydrogen is able to remove the oxygen from many hot metallic oxides with formation of water. In such reactions hydrogen is said to *reduce* the oxide to the metal, and hydrogen is spoken of as a *reducing agent.*

A reducing agent may be defined as a *substance which is capable of removing oxygen from a compound.* Other reducing agents will be met with in future chapters.

QUESTIONS.—CHAPTER X.

1. What metals decompose water (*a*) at ordinary temperature, (*b*) at red heat? Give equations showing the nature of the reaction in each case.
2. If you desire to obtain hydrogen in as pure a condition as possible, what method would you adopt?
3. If you desire to prepare moderately pure hydrogen in large quantities, what method would you adopt?
4. Write down equations showing the action of iron and magnesium respectively on dilute sulphuric acid.
5. Devise three experiments suitable for illustrating in a striking manner the extreme lightness of hydrogen.
6. State the chief properties of hydrogen, dividing them into (*a*) physical properties and (*b*) chemical properties.
7. Name three metallic and three non-metallic hydrides, and give their formulæ.
8. Explain, with examples, what is meant by a *reducing agent.*

CHAPTER XI.

OXYGEN AND OZONE.

OXYGEN, O_2.

73. Occurrence.—Oxygen is the most widely distributed of the elements; it constitutes about one-half of the earth's crust. Air contains about 20 per cent. of oxygen, water nearly 90 per cent., and the great majority of minerals consist largely of this element.

74. Methods of Preparation.—(1) We have already seen in Exp. 21 that oxygen can be prepared by strongly heating potassium chlorate. The course of the reaction is somewhat complex. Decomposition commences at about 370° C., the changes represented in the two following equations taking place simultaneously:—

$$4\ KClO_3 = 3\ KClO_4 + KCl$$
$$2\ KClO_3 = 2\ KCl + 3\ O_2.$$

At higher temperature the perchlorate is decomposed thus:—

$$KClO_4 = KCl + 2\ O_2.$$

It is found that if the potassium chlorate is intimately mixed with certain substances in a fine state of division, the decomposition takes place at a much lower temperature and with greater regularity. Examples of such substances are manganese dioxide, cupric oxide and finely-divided platinum. They are found to be unaltered at the termination of the process, and are called *catalytic agents*, the phenomenon being termed *catalysis*.

In practice manganese dioxide is the substance commonly used, and the laboratory method for the preparation of oxygen which is not required particularly pure, consists in heating an intimate mixture of potassium chlorate with about one-third of its weight of manganese dioxide.

Exp. 84.—Weigh out about 10 grammes of potassium chlorate and 3 grammes of manganese dioxide, and grind them together in a mortar till they are thoroughly mixed. Introduce the mixture into a small round-bottomed flask, and set up the apparatus shown in Fig. 5, § 16. On heating the mixture to about 300° C., *i.e.* a temperature considerably below the melting-point of potassium chlorate, oxygen is rapidly evolved and may be collected over water.

The change which takes place when manganese dioxide is used may be represented by the equation—

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

It should be mentioned that no potassium perchlorate is formed when a catalytic agent is used in the decomposition of potassium chlorate.

(2) Many oxides on heating evolve oxygen. Two of these—mercuric oxide, HgO, and red lead, Pb_3O_4—have already been used to prepare the gas. The equations representing their decomposition on heating are—

$$\begin{aligned} 2\,HgO &= 2\,Hg + O_2. \\ 2\,Pb_3O_4 &= 6\,PbO + O_2. \end{aligned}$$

Other oxides which lose oxygen on heating are silver oxide, Ag_2O, chromium trioxide, CrO_3, lead peroxide, PbO_2, barium dioxide, BaO_2, and manganese dioxide, MnO_2—

$$\begin{aligned} 2\,Ag_2O &= 4\,Ag &&+ O_2. \\ 4\,CrO_3 &= 2\,Cr_2O_3 &&+ 3\,O_2. \\ 2\,PbO_2 &= 2\,PbO &&+ O_2. \\ 2\,BaO_2 &= 2\,BaO &&+ O_2. \\ 3\,MnO_2 &= Mn_3O_4 &&+ O_2. \end{aligned}$$

In the case of manganese dioxide the temperature required is much higher than that used in the preparation of oxygen from potassium chlorate and manganese dioxide.

(3) Peroxides on heating with strong sulphuric acid yield oxygen—

$$2\,MnO_2 + 2\,H_2SO_4 = 2\,MnSO_4 + 2\,H_2O + O_2.$$

Manganese dioxide. Manganese sulphate.

$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O + O_2.$$

Lead peroxide. Lead sulphate.

(4) Many salts which contain a large percentage of oxygen are decomposed on heating, either alone or in some cases with strong sulphuric acid, with evolution of oxygen. We have already discussed the action of heat on one such salt—potassium chlorate. Another example is potassium nitrate (KNO_3) which on heating loses oxygen and becomes converted into potassium nitrite (KNO_2)—

$$2\,KNO_3 = 2\,KNO_2 + O_2.$$

As illustrations of salts which evolve oxygen on heating with strong sulphuric acid we may take potassium permanganate ($KMnO_4$) and potassium bichromate ($K_2Cr_2O_7$)—

$$\begin{aligned}4\,KMnO_4 + 8\,H_2SO_4 &= 4\,KHSO_4 + 4\,MnSO_4 + \\ &\qquad 6\,H_2O + 5\,O_2.\\ 2\,K_2Cr_2O_7 + 10\,H_2SO_4 &= 4\,KHSO_4 + 2\,Cr_2(SO_4)_3 + \\ &\qquad 8\,H_2O + 3\,O_2.\end{aligned}$$

(5) If bleaching powder is mixed with certain oxides such as cobalt oxide (CoO), or cupric oxide (CuO), and the mixture made into a paste with water, a ready supply of oxygen is obtained on gently heating. Here again the oxide plays the part of a catalytic agent.

Bleaching powder is a mixture of a substance, $CaOCl_2$, with slaked lime, $Ca(OH)_2$. On treating as above described the following decomposition takes place:—

$$2\,CaOCl_2 = 2\,CaCl_2 + O_2.$$

75. Manufacture of Oxygen.—At the present time oxygen is manufactured by liquefying air and then distilling off the more volatile nitrogen. Until recently, however, a process known as *Brin's process* was used. This depends upon the fact that when baryta, BaO, is heated to *dull redness* in air it takes up oxygen and is converted into the dioxide, BaO_2, which at a *bright red heat* loses the oxygen which it had taken up, and is transformed again into baryta—

$$2\,BaO + O_2 = 2\,BaO_2.$$

$$2\,BaO_2 = 2\,BaO + O_2.$$

The original proposition of Boussingault to prepare oxygen on the large scale in this way failed owing to certain difficulties. These were, however, finally overcome by the Brin process. In this process the same reaction was made use of, but it was found that in order to make the process a continuous one the following conditions must be attended to :—

(*a*) the air must be freed from CO_2 and excessive moisture.

(*b*) the baryta must be so prepared as to obtain it in a firm and yet porous condition. It is obtained in the best condition by heating barium nitrate.

(*c*) the temperatures employed in the oxidation of the baryta and its subsequent deoxidation must be kept as low as possible.

An important modification of the original process was also made under which it was no longer necessary to work alternately at higher and lower temperatures. By means of a force-pump the air was brought into contact with the heated baryta under a pressure of about 15 lbs. to the square inch When sufficient time had elapsed to allow of conversion into barium peroxide connection was made with an exhaust pump, and the pressure reduced to about one-tenth of an atmosphere. Under so low a pressure the barium peroxide was decomposed at the same temperature which under higher pressures sufficed to form it. Instead, therefore, of varying the temperatures it is only necessary to establish high and low pressure alternately, the periods of operation being about a quarter of an hour.

The baryta was contained in a number of iron cylinders connected together by pipes and placed vertically in a furnace and heated by "producer gas." The working was practically continuous and only needed to be interrupted about every six months for the purpose of breaking up the baryta and adding a little fresh material.

76. **Properties.**—Oxygen is a colourless, odourless gas only slightly soluble in water, 1 c.c. of which dissolves 0·0489 c.c. of the gas at 0° C. and 0·034 c.c. at ordinary temperatures. The weight of 1 c.c. of oxygen under standard conditions of temperature and pressure, *i. e.* its absolute density, is 0·001429 gramme. Since 1 c.c. of hydrogen weighs 0·00009 gramme under standard conditions, the relative density of oxygen taking hydrogen as unity is $\frac{0\cdot001429}{0\cdot00009} = 15\cdot88$. Taking air as unity the relative density of oxygen is $\frac{0\cdot001429}{0\cdot0012935} = 1\cdot106$ (for 1 c.c. of air under standard conditions weighs ·0012935 gramme), *i. e.* oxygen is slightly heavier than air.

As has already been stated, the atomic weight of oxygen is usually taken as the standard with the value 16. Since the molecule of oxygen contains two atoms the molecular weight of oxygen is 2 × 16 = 32.

The distinguishing feature of oxygen is that it combines readily with nearly all the elements, and often with such energy that the union is accompanied by manifestation of light and heat. This phenomenon is termed "combustion," and oxygen is consequently a *powerful supporter of combustion.* A glowing splinter of wood, if plunged into oxygen, immediately bursts into flame, a property which is only shown by one other gas, nitrous oxide.

Experiments have already been described in Chapter II. illustrating the properties of oxygen, and the student should refer back to them. The chemical changes which take place when sulphur, phosphorus, carbon and iron burn in oxygen are represented by the following equations:—

$$S + O_2 = \underset{\text{Sulphur dioxide.}}{SO_2.}$$

$$P_4 + 5\,O_2 = \underset{\text{Phosphorus pentoxide.}}{2\,P_2O_5.}$$

$$C + O_2 = \underset{\text{Carbon dioxide.}}{CO_2.}$$

$$3\,Fe + 2\,O_2 = \underset{\substack{\text{Magnetic oxide of iron,}\\ \text{or triferric tetroxide.}}}{Fe_3O_4.}$$

Other metals, besides iron, burn brightly in oxygen; thus sodium is converted into sodium peroxide, Na_2O_2, magnesium into magnesium oxide, MgO, and so on.

We have also seen, however, that oxidation can go on at ordinary temperatures. Thus, iron rusts in moist air forming ferric oxide, Fe_2O_3, combined with some water; phosphorus fumes and gives out a faint luminosity in air forming phosphorous oxide, P_4O_6, and other compounds. Organic matter and some mineral substances, such as iron pyrites, also undergo oxidation in the air at ordinary temperatures. This phenomenon of oxidation without the application of heat is often termed *slow combustion*, though the usual manifestations of combustion, viz. the production of light and sensible heat, are, as a rule, absent. As a matter of fact, heat is being given out during these reactions, but so slowly that its production is not apparent.

Oxygen plays an important part in vital processes, both in the animal and vegetable organisms, transforming carbonaceous substances ultimately into carbon dioxide and hydrogenous substances into water. This accounts for the fact that exhaled breath always contains carbon dioxide and water vapour. It is the heat evolved during these processes which maintains the body of an animal at the necessary temperature.

77. **Oxidising Agents.**—An *oxidising agent is a substance which is able to give up oxygen to other substances.** Oxygen itself is therefore the oxidising agent *par excellence.* The substance which combines with the oxygen is said to be *oxidised*, or to undergo a process of *oxidation.* It will be noticed that the definition of an oxidising agent given above is the reverse of the definition of a reducing agent given in § 72. The processes of oxidation and reduction usually go on together, the oxidising agent being reduced and the reducing agent oxidised. Thus when nitric acid, which is an oxidising agent, acts on metallic tin, which is a reducing agent, the acid is reduced to various oxides of nitrogen, and the tin is oxidised to stannic oxide (SnO_2).

78. **The Oxides.**—With the exception of fluorine and bromine, all the elements combine with oxygen forming *oxides.* These have already been classified in Chapter VII., but it will be well to again state the three classes before going on to consider them more closely. They are—

(1) Acidic oxides.
(2) Basic oxides.
(3) Peroxides.

Acidic Oxides.—It was Lavoisier who first showed that the oxides of certain elements (viz. the non-metals), when dissolved in water, form acids The following equations represent the reactions which take place when some of these oxides, called *acidic oxides,* combine with water :—

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* The definition of the term *oxidation* is often extended to include any increase in the ratio of the non-metallic to the metallic part of a substance. Thus the conversion of stannous chloride ($SnCl_2$) into stannic chloride ($SnCl_4$) by chlorine is spoken of as the oxidation of stannous chloride to stannic chloride. In such cases the compounds are considered as *derivatives of the corresponding oxides.* A corresponding extension will have to be made in the definition of an *oxidising agent.* Similar extensions are also made in the definitions of *reduction* and *reducing agent.*

$$\underset{\text{Sulphur dioxide.}}{SO_2} + H_2O = \underset{\text{Sulphurous acid.}}{H_2SO_3.}$$
$$\underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4.}$$
$$\underset{\text{Phosphorus pentoxide.}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric acid.}}{2\ HPO_3.}$$
$$\underset{\text{Carbon dioxide.}}{CO_2} + H_2O = \underset{\text{Carbonic acid.}}{H_2CO_3.}$$
$$\underset{\text{Nitrogen pentoxide.}}{N_2O_5} + H_2O = \underset{\text{Nitric acid.}}{2\ HNO_3.}$$

Basic Oxides.—These are the oxides of the metals which on treatment with acids yield salts and water *only* (cf. peroxides). A few of them are soluble in water, combining with it to form hydroxides. Such are potassium monoxide, K_2O, calcium monoxide or quick-lime, CaO, and barium monoxide, BaO. With water these form, respectively, potassium hydroxide or caustic potash, KOH, calcium hydroxide or slaked lime, $Ca(OH)_2$, and barium hydroxide, $Ba(OH)_2$.

$$K_2O + H_2O = 2\ KOH.$$
$$CaO + H_2O = Ca(OH)_2.$$
$$BaO + H_2O = Ba(OH)_2.$$

The majority of the metallic oxides are, however, insoluble in water, and their hydroxides can only be obtained indirectly. Examples of insoluble oxides are zinc oxide, ZnO, and mercuric oxide, HgO.

Oxides which are both Acidic and Basic.—There are some oxides which at one time play the part of basic oxides and at another of acidic oxides, and it is only by considering the nature of the salt in which they occur that we can say in which capacity they are acting. For instance, sodium stannate, Na_2SnO_3, is formed from soda and oxide of tin, the oxide of tin being the acid constituent, whilst in stannic sulphate, $Sn(SO_4)_2$, the oxide of tin is the basic constituent.

Peroxides.—These are oxides which contain a high percentage of oxygen and do not form corresponding salts with acids. They may be divided into two classes. (1) those which form hydrogen peroxide with dilute mineral acids; (2) those which do not. Examples of Class (1) are barium peroxide, BaO_2, and sodium peroxide, Na_2O_2; and of Class (2) manganese dioxide, MnO_2, and lead peroxide, PbO_2. All peroxides on heating with strong sulphuric acid evolve oxygen and form sulphates corresponding to a lower oxide of the metal. Thus barium peroxide forms barium sulphate corresponding to BaO, and lead peroxide forms lead sulphate corresponding to PbO.

$$2\,BaO_2 + 2\,H_2SO_4 = 2\,BaSO_4 + 2\,H_2O + O_2.$$
$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O + O_2.$$

Exp. 85.—Heat gently small quantities of barium peroxide and lead peroxide with strong sulphuric acid in test-tubes, and test the evolved gas for oxygen.

A peroxide belonging to Class (2) evolves *chlorine* on heating with strong hydrochloric acid, and is converted into the chloride corresponding to a lower oxide;

$$e.g.\ PbO_2 + 4\,HCl = PbCl_2 + 2\,H_2O + Cl_2.$$

One belonging to Class (1), on the other hand, yields *oxygen* and the chloride derived from a lower oxide on similar treatment;

$$e.g.\ 2\,BaO_2 + 4\,HCl = 2\,BaCl_2 + 2\,H_2O + O_2.$$

79. **Proof that Oxides contain Oxygen.**—The following method may be adopted to prove that oxides which do not evolve oxygen on heating, and are not reduced on heating in hydrogen (*e.g.* quicklime), contain oxygen:—

Exp. 86.—Introduce a layer of quicklime (CaO) into a tube similar to that used in Exp. 31. Arrange the tube and accessories as in Fig. 13, but connect it with an apparatus for preparing dry hydrochloric acid (see Exp. 119) instead of hydrogen. On heating the quicklime and passing dry hydrochloric acid water is formed and drops over into the watch-glass, thus proving that quicklime contains oxygen, for we know that dry hydrochloric acid does not, since it is produced by the direct combination of the elements hydrogen and chlorine.

CaO	+	$2HCl$	=	$CaCl_2$	+	H_2O.
Quicklime.		Hydrochloric acid.		Calcium chloride.		Water.

OZONE, O_3.

80. Under certain conditions oxygen is found to possess a peculiar odour similar to that observed in the neighbourhood of an electrical machine during electrical discharge; and it differs from ordinary oxygen in its physical and chemical properties. This modified form of oxygen is termed ozone.

Exp. 87.—Preparation and Properties of Ozone.—Ozone occurs in the oxygen produced during the electrolysis of water, and is produced in small quantity during the slow oxidation of phosphorus (see § 76), but it is most conveniently obtained by passing "a silent discharge" from two Grove's cells and an induction coil*, through dry oxygen. For this purpose the apparatus shown (Fig. 28) may be used. An outer tube A B ending below in a narrower portion bent into a U-tube, is provided with two stopcocks, and an inner tube of somewhat smaller diameter, closed at the bottom, and sealed in at A. The outer tube is surrounded throughout its whole length by a coil of platinum wire, and the inner tube is filled with dilute sulphuric acid, and another platinum wire dips into this. The stopcocks are opened, and concentrated sulphuric acid is poured into the U-tube, which serves as a gauge, and dry oxygen passed through the annular space till the air is swept out. Now close the stopcocks and connect the two platinum wires to the terminals of the induction coil. The temperature of the apparatus should be kept constant during the experiment, and this may easily be effected by surrounding it with water at the same temperature as the room. After passing the silent discharge for a little while some of the oxygen contained in the space between the tubes will have been converted into ozone, and the following observations may be made :—

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* The exact nature of this electrical phenomenon (produced by the apparatus described below) is not understood; it appears to be doubtful whether any true electric current passes through the oxygen or not.

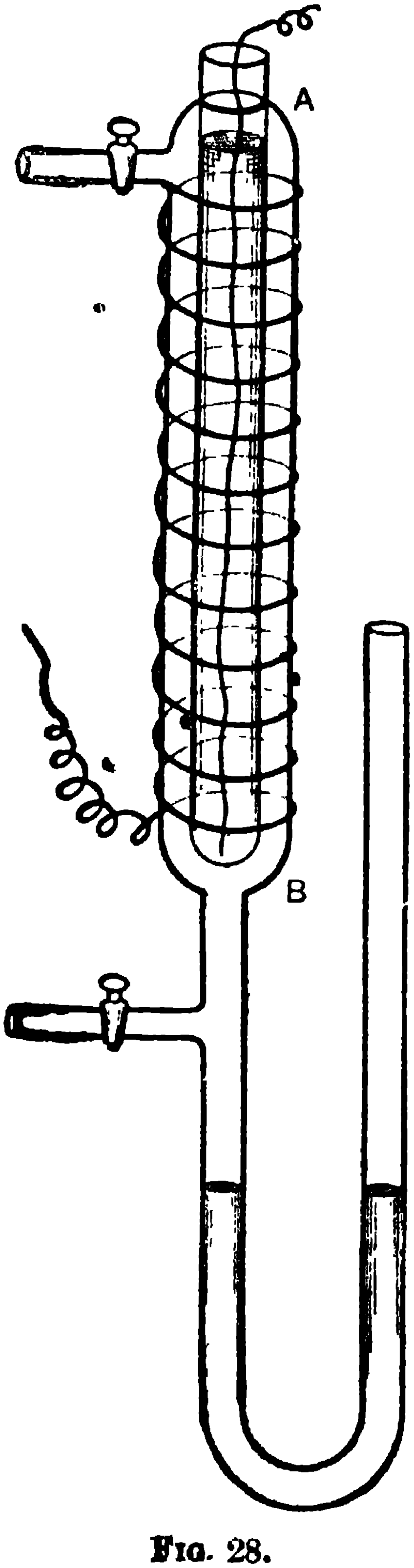

Fig. 28.

(1) The volume of the gas in the annular space diminishes, as will be indicated by the sulphuric acid in the gauge. By determining beforehand the relative volume of the space in which the oxygen is confined, and that of a given length of the U-tube, an approximate estimate may be made of the amount of contraction.

(2) Attach a tube at the upper stopcock, open both stopcocks, and drive out some of the ozonised oxygen at the lower one, holding a paper dipped in solution of potassium iodide near the outlet. The paper will turn brown from the liberation of iodine, the ozone being transformed into ordinary oxygen.

$$2\,KI + O_3 + H_2O = 2\,KOH + O_2 + I_2.$$

(3) Bleach indigo or moist litmus in a similar way.

(4) Note the odour of the ozone.

(5) Put a globule or two of mercury in a small flask and pass ozonised oxygen into the flask. On shaking, the mercury is superficially oxidised, loses its convexity of

surface, and spreads out in a film on the walls of the flask.

(6) Expel the ozonised oxygen from the lower stopcock through a glass tube about 20 cms. long, heating the tube to dull redness ; at 250° C. ozone is transformed into oxygen, and after heating, a test made as in (2) should give no liberation of iodine.

The above observations show the great chemical activity of ozone, and the features by which it is distinguished from oxygen, for ordinary oxygen does not bleach, nor does it oxidise mercury or liberate iodine from potassium iodide at ordinary temperatures ; ozone also readily attacks rubber tubing, and rubber connections should therefore be avoided in making experiments with the gas ; it may be added that ozone is readily taken up by turpentine and certain other essential oils.

By using the method described above, not more than 8 or at most 10 per cent. of the oxygen can be transformed into ozone. If, however, ozonised oxygen is passed through a tube surrounded by liquid oxygen, the ozone condenses to a blue liquid, which boils at $-110°$ C. with formation of a blue explosive gas.

81. **Composition of Ozone.**—The density of pure ozone prepared in this way has been shown by Ladenburg to be 24 ($H = 1$). Its molecular weight, therefore, is $2 \times 24 = 48$. Now since the atomic weight of oxygen is 16, a molecule of ozone must consist of three atoms of oxygen, for $3 \times 16 = 48$. This explains why there is a diminution of volume when oxygen is converted into ozone, for *three* molecules of oxygen (O_2) give rise to only *two* molecules of ozone (O_3)—

$$3\,O_2 = 2\,O_3.$$

Applying Avogadro's hypothesis, it follows that three volumes of oxygen should give rise to two volumes of ozone. This may be proved experimentally in the following manner :—

The contraction in volume on ozonising a known volume of oxygen is measured. The ozone is then absorbed by turpentine, and the further diminution in volume noted. Thus suppose in an experiment 100 vols. of oxygen contracted to 97 vols. on being ozonised, and absorption with turpentine caused a further diminution of volume to 91 vols. Then we have—

Volume of ozone ... ... = (97 − 91 vols.) = 6 vols.
,, ,, oxygen from which it was formed = (100 − 91 vols.) = 9 vols.

The ozone was therefore formed by the condensation of 9 volumes of oxygen into the space of 6 volumes, or 3 volumes of oxygen condense to produce 2 volumes of ozone.

82. **Allotropy.**—Oxygen and ozone afford the first example of a phenomenon exhibited by several elements, namely, of existing in two or more forms with different physical and to some extent chemical properties. The less common forms are said to be *allotropic modifications* of the commonest; thus ozone is an allotropic modification of oxygen. When one allotropic modification of an element is converted into another, heat is invariably either evolved or absorbed; if there are two modifications of an element A and B, and if heat is evolved when A is converted into B, it will be absorbed when B is converted into A. Now oxygen is changed into ozone with absorption of heat. It is a general rule that bodies produced with absorption of heat are decomposed very easily, giving out the heat absorbed in their formation. This explains the greater activity of ozone as compared with oxygen. The molecule of ozone readily breaks down into a molecule of oxygen and a free atom of oxygen, with evolution of heat—

$$O_3 = O_2 + O.$$

This free atom of oxygen immediately attacks any oxidisable substance within reach, such as mercury, potassium iodide, etc., and if no such substance is present the free oxygen atoms unite to form stable molecules of oxygen.

The reason that a free atom of oxygen is so much more active than a molecule of oxygen is that before the latter can enter into a chemical reaction it must be broken down into two atoms of oxygen, and it requires the expenditure of a considerable amount of energy to bring this about.

83. **Nascent state.**—An element when just liberated from a compound is said to be *nascent* (*nascor*, I am born), and in general it shows special activity when in this state. This will be understood from what has just been said with regard to oxygen, for an element is always in the atomic condition when just set free from combination.

Another example of the greater activity of an element in the nascent state is afforded by the following experiment with hydrogen:—

Exp. 87a.—Prepare hydrogen by the action of granulated zinc on dilute sulphuric acid and convey it by means of a delivery tube into a beaker containing a solution of potassium permanganate (pink). Introduce some of the permanganate into a second beaker and add dilute sulphuric acid and zinc. Note that in the latter case the colour of the permanganate gradually disappears, whereas in the former case it remains unchanged.

The explanation is that when the hydrogen is produced *in contact with* the potassium permanganate, as in the second case, it is in the *nascent state* (H) and reduces the permanganate in presence of sulphuric acid with formation of manganous sulphate, which is practically colourless in dilute solution.

$$Zn + H_2SO_4 = ZnSO_4 + \underset{\text{Nascent}}{2\,H}$$

$$2\,KMnO_4 + 3\,H_2SO_4 + \underset{\text{Nascent}}{10\,H}$$

$$= K_2SO_4 + \underset{\substack{\text{Manganous}\\\text{sulphate}}}{2\,MnSO_4} + 8\,H_2O.$$

When, on the other hand, the hydrogen is produced *externally* and then passed into the permanganate solution, as in the first case, it is in the *molecular state* (H_2) and exercises no reducing action.

QUESTIONS.—CHAPTER XI.

1. Describe the laboratory method of preparing oxygen, and sketch the apparatus used.
2. Give a list of oxides which evolve oxygen on heating, and represent the decompositions which they undergo by equations.
3. Express by equations the changes which take place when the following substances are heated: (1) a mixture of manganese dioxide and strong sulphuric acid, (2) potassium nitrate, (3) a mixture of potassium permanganate and strong sulphuric acid.
4. How may oxygen be obtained from bleaching powder?
5. State how baryta may be used as a means of obtaining oxygen from the atmosphere.
6. Give instances of the formation of oxides by the action of oxygen on elementary substances, (*a*) where such action takes place at ordinary temperatures, (*b*) where heat must be applied in order to start the reaction
7. What takes place when the products of combustion of carbon, sulphur and phosphorus are respectively brought into contact with water?
8. What is meant by *slow combustion*?
9. Explain the term *oxidising agent.*
10. What is an *oxide*? Give instances of oxides of the metals which are soluble in water, and of oxides which are insoluble in water.
11. Given metallic magnesium and sulphuric acid, how would you prepare a specimen of Epsom salts ($MgSO_4 . 7 H_2O$)?
12. Give examples showing that the same oxide may at one time function as the acidic constituent of a salt, and at another time as the basic constituent.
13. How do the peroxides differ (*a*) in composition, (*b*) in their chemical deportment, from ordinary oxides?
14. How would you prove that lime contains oxygen?

CHAPTER XII.

ACIDS—BASES—SALTS—TYPES OF CHEMICAL CHANGE.

84. **Acids.**—A brief historical sketch of the use of the term "acid" will be of value, before we consider the meaning assigned to it at the present time. The properties originally associated with an "acid" were—

(1) Sourness (Gk. ὀξύς, L. *acidus*, sour).

(2) Solubility in water.

(3) Power of removing the alkaline properties of such substances as caustic soda and caustic potash.

(4) Power of changing the colour of certain blue vegetable substances (such as litmus) to red.

It was found, however, that certain substances not included under the head of acids possessed all these properties. Thus alum has a sour taste, is soluble in water, deprives caustic soda of its alkaline properties, and turns blue litmus red.

After Lavoisier's discovery that the compounds produced by burning certain elements in oxygen yield acids with water, it was assumed that *oxygen was the essential constituent of an acid.* This view was overthrown when it was proved that certain acids such as hydrochloric acid (HCl) and sulphuretted hydrogen (H_2S) do not contain oxygen at all. A distinction was then made between acids which do contain oxygen and those which do not. The former were (and still are) called *oxyacids* and the latter *hydracids*.

It was Davy who first showed that *hydrogen* and not oxygen is the essential constituent of an acid. He was led to this conclusion by the discovery that iodic anhydride (I_2O_5), which contains oxygen but no hydrogen, is not an acid, but on treating it with water (*i. e.* with a compound of hydrogen and oxygen) it acquires acid properties. About the same time Dulong arrived at a similar conclusion as a result of studying the action of metallic oxides on oxalic acid. He considered that when an acid was treated with a metallic oxide the metal of the oxide replaced the hydrogen of the acid with formation of a *salt*.

At the present time an acid may be defined as a substance which

(1) contains hydrogen, part or all of which is replaced by a metal when the acid is treated with the metal itself (not in all cases), or with an oxide or hydroxide of the metal;
(2) usually has a sour taste;
(3) is usually corrosive;
(4) changes the colour of certain blue vegetable substances to red, or in certain cases (carbonic acid, boric acid) to a claret colour.

Clause (1) of this definition excludes such substances as alum which fulfil the remaining conditions.

A very good and concise definition is the following:—*An acid is a substance containing hydrogen part or all of which it exchanges for potassium (or sodium) when brought in contact with caustic potash (or caustic soda).*

85. Salts.—A *salt* may be defined as a substance produced by the replacement of part or all of the hydrogen of an acid by a metal or group of elements (such as NH_4) which takes the place of a metal.

Thus when zinc dissolves in hydrochloric acid the zinc replaces the hydrogen of the acid forming the salt zinc chloride, $ZnCl_2$—

$$\underset{}{Zn} + \underset{\text{Acid.}}{2\,HCl} = \underset{\text{Salt.}}{ZnCl_2} + H_2.$$

Again, when one molecule of caustic soda, NaOH, reacts with one molecule of sulphuric acid, H_2SO_4, part of the hydrogen of the acid is replaced by the metal sodium forming the salt acid sodium sulphate, $NaHSO_4$—

$$NaOH + \underset{\text{Acid.}}{H_2SO_4} = \underset{\text{Salt.}}{NaHSO_4} + H_2O.$$

86. **Bases.**—A *base* may be defined as a *substance which with an acid produces a salt and water only.* The substances included as bases adopting this definition are basic oxides and hydroxides of the metals or of a group of elements equivalent to a metal (*e. g.* NH_4). Thus, hydrochloric acid reacts with the base calcium oxide, to produce the salt calcium chloride and water—

$$\underset{\text{Base.}}{CaO} + \underset{\text{Acid.}}{2\,HCl} = \underset{\text{Salt.}}{CaCl_2} + \underset{\text{Water.}}{H_2O}.$$

Again, sulphuric acid reacts with the base zinc hydroxide, to produce the salt zinc sulphate and water—

$$\underset{\text{Base.}}{Zn(OH)_2} + \underset{\text{Acid.}}{H_2SO_4} = \underset{\text{Salt.}}{ZnSO_4} + \underset{\text{Water.}}{2\,H_2O}.$$

Once again, nitric acid reacts with the base ammonium hydroxide, to produce the salt ammonium nitrate, and water—

$$\underset{\text{Base.}}{NH_4OH} + \underset{\text{Acid.}}{HNO_3} = \underset{\text{Salt.}}{NH_4NO_3} + \underset{\text{Water.}}{H_2O}.$$

Usually, certain substances are, for convenience, called bases which do not conform to the above definition. These are ammonia (NH_3), and its numerous derivatives (such as aniline) which are met with amongst the compounds of carbon. These substances form salts with acids, but without the production of water. Thus ammonia with hydrochloric acid gives the salt ammonium chloride—

$$NH_3 + \underset{\text{Acid.}}{HCl} = \underset{\text{Salt.}}{NH_4Cl}.$$

It is unfortunate that a separate name has not been adopted for these substances.

Alkalies.—Those bases which are soluble in water, such as caustic soda and lime, are called *alkalies;* they possess special properties, which may be illustrated by the following experiment:—

Exp. 88.—Take some caustic soda and lime, and moisten them with water. Add to them (1) litmus, (2) olive oil, and shake the mixtures. In both cases the litmus is turned blue, and the oil disappears gradually, from the formation of soap. The caustic soda solution feels soapy to the touch, and has a taste like washing soda.

87. Basicity of Acids.—Some acids can only produce one salt by interaction with a given base, whereas others can form two, three, or even four different salts. This may be studied by experiment.

Exp. 89.—Measure out 50 c.cs. of dilute hydrochloric acid into an evaporating basin, and gradually add dilute caustic potash to it from a graduated cylinder, until the solution is neutral to litmus. Note the volume of caustic potash used. Now measure out another 50 c.cs. of the acid into a second evaporating basin, and add to it half the quantity of caustic potash required to neutralise it. Evaporate the two solutions down to small bulk, and allow to cool. Crystals will separate out from each; drain away the mother liquor from them, and dry between blotting-paper. Examine the two lots of crystals. You will notice that they are quite similar in appearance.

Exp. 90.—Proceed exactly as in the last experiment, but use dilute sulphuric acid instead of hydrochloric acid. Again examine the two sets of crystals. This time they differ in appearance.

From these two experiments we learn that hydrochloric acid only gives one salt with potash, whereas sulphuric acid gives two salts. On comparing the formulæ of these acids —HCl, H_2SO_4—it will be noticed that whilst the former only contains one atom of hydrogen in its molecule the latter has two. When we neutralised hydrochloric acid with caustic potash, we replaced the hydrogen atom of each of the molecules of acid by potassium according to the equation—

$$KOH + HCl = KCl + H_2O$$

and when we only added half the quantity of potash required for neutralisation, we replaced the hydrogen atoms of half the HCl molecules by potassium according to the same equation. The other half of the HCl molecules remained unattacked.

On neutralising sulphuric acid with caustic potash, the two hydrogen atoms of each molecule of the acid were replaced by potassium according to the equation—

$$2\,KOH + H_2SO_4 = K_2SO_4 + 2\,H_2O.$$

When, however, only half the quantity of potash was used only one atom of hydrogen in each molecule of the acid was replaced by potassium, the equation being—

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

No acid remained unacted upon here, as was the case with hydrochloric acid. If we had gone further and used only one-third the quantity of potash required to neutralise the sulphuric acid, we should not have obtained another new salt. The reaction would have proceeded as in the last equation, and some of the acid would have remained unacted upon.

Phosphoric acid contains three atoms of hydrogen, and gives rise to three classes of salts according as one, two or all of these atoms are replaced by a metal—

$$\begin{aligned} H_3PO_4 &+ NaOH = NaH_2PO_4 + H_2O. \\ H_3PO_4 &+ 2\,NaOH = Na_2HPO_4 + 2\,H_2O. \\ H_3PO_4 &+ 3\,NaOH = Na_3PO_4 + 3\,H_2O. \end{aligned}$$

It must not be assumed that all the atoms of hydrogen in an acid are necessarily replaceable by a metal; this is often not the case. For instance, acetic acid has the formula $C_2H_4O_2$, but only one of the four hydrogen atoms can be replaced by a metal. To indicate this we may write the formula $C_2H_3O_2{\cdot}H$, showing that one hydrogen atom differs in properties from the others. On neutralising acetic acid with caustic soda the following change takes place:—

$$C_2H_3O_2{\cdot}H + NaOH = C_2H_3O_2{\cdot}Na + H_2O.$$

The number of atoms of hydrogen replaceable by a metal contained in one molecule of an acid, is termed the *basicity* of the acid. Thus the basicity of hydrochloric acid is 1, of sulphuric acid 2, of phosphoric acid 3, and of acetic acid 1; or, in other words, hydrochloric and acetic acids are *monobasic*, sulphuric acid is *dibasic*, and phosphoric acid is *tribasic*.

88. **Normal and Acid Salts.**—Salts produced by the replacement of the whole of the replaceable hydrogen of an acid by metals are called *normal* salts. Potassium chloride (KCl), normal potassium sulphate (K_2SO_4), trisodium phosphate, or normal sodium phosphate (Na_3PO_4), and sodium acetate ($C_2H_3O_2 \cdot Na$) belong to this class. When only part of the replaceable hydrogen of an acid is replaced by metals, the resulting salts are known as *acid salts*. Such are potassium hydrogen sulphate or acid potassium sulphate ($KHSO_4$), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4).

It should be noticed that normal salts are not by any means always *neutral* to litmus and similar indicators. Some of them show an acid reaction (*e. g.* copper sulphate, $CuSO_4$), whilst others show an alkaline reaction (*e. g.* normal sodium carbonate, Na_2CO_3). Sodium chloride and normal potassium sulphate are examples of normal salts which are neutral.

So, again, though many acid salts are *acid* to litmus, this is not true for all. Disodium hydrogen phosphate, for instance, shows an alkaline reaction.

89. **Basic Salts.**—On considering the formulæ of the bases potassium hydroxide, KOH, lead hydroxide, $Pb(OH)_2$, and bismuth hydroxide, $Bi(OH)_3$, it will be noticed that they differ in the number of hydroxyl (OH) groups which they contain. The question arises, whether these OH groups can be successively replaced by the acid group of an acid (*e. g.* NO_3, the acid group of nitric acid) in the same way that the hydrogen atoms of a polybasic acid can be successively replaced by a metal. This is found to be the case very frequently, and, just as the basicity of an acid is

determined by the number of replaceable hydrogen atoms its molecule contains, so the *acidity* of a base is determined by the number of hydroxyl groups it contains. (We will leave out of consideration for the present the case of *oxides*, dealing only with *hydroxides*.) Thus KOH is a *monacid* base, $Pb(OH)_2$ is a *diacid* base, and $Bi(OH)_3$ is a *triacid* base.

When only part of the OH groups of a base are replaced by an acid group, the salt formed is termed a *basic salt*. Thus $Pb(OH)_2$ gives basic lead nitrate, $Pb(OH)(NO_3)$, by the replacement of one of its hydroxyl groups by the acidic group NO_3 (from HNO_3). When both hydroxyl groups are replaced, normal lead nitrate, $Pb(NO_3)_2$, is formed.

Basic salts may be made in three ways—

(1) By treating the base with insufficient acid to convert the whole of the base into the normal salt.

Thus, on treating a molecule of bismuth hydroxide with one of nitric acid, only one of the OH groups of the base is replaced by NO_3—

$$Bi(OH)_3 + HNO_3 = Bi(OH)_2NO_3 + H_2O.$$

(2) By treating the normal salt with excess of water.

Normal bismuth nitrate is converted by the action of water into the same basic salt that was obtained in (1)—

$$Bi(NO_3)_3 + 2\ H_2O = Bi(OH)_2\ NO_3 + 2\ HNO_3.$$

(3) By mixing the normal salt and the free base.

Thus, on mixing normal lead acetate and lead hydroxide, basic lead acetate is produced—

$$Pb(C_2H_3O_2)_2 + Pb(OH)_2 = 2\ Pb(OH)(C_2H_3O_2).$$

Basic salts can be derived from *oxides* as well as from hydroxides. One atom of oxygen is equivalent in combining capacity to two hydroxyl (OH) groups. Thus, CaO (quicklime), on treatment with water, forms $Ca(OH)_2$, slaked lime. Hence a basic oxide having the formula MO, where M is a metal, will be a *diacid* base; for it will be able to neutralise as much acid as a basic hydroxide which contains *two* hydroxyl groups. Thus quicklime, CaO, and slaked lime, $Ca(OH)_2$, both neutralise two molecules of nitric acid—

$$\begin{aligned} CaO + 2\,HNO_3 &= Ca(NO_3)_2 + H_2O. \\ Ca(OH)_2 + 2\,HNO_3 &= Ca(NO_3)_2 + 2\,H_2O. \end{aligned}$$

An example of a basic salt derived from an oxide is bismuth oxychloride, BiOCl. This may be obtained by the action of excess of water on bismuth trichloride—

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

It should be pointed out that all basic salts can be considered as compounds of normal salts with the free base, and in many cases this is the most convenient way of treating them; thus white lead, or basic lead carbonate, is formulated $2\,PbCO_3 + Pb(OH)_2$, basic mercuric sulphate is $HgSO_4 + 2\,HgO$. Reverting to the examples given above, we may write their formulæ out again on the plan just mentioned, and show as below that the two sets of formulæ are equivalent—

$$\begin{aligned} \text{Basic lead nitrate} &= Pb(OH)_2 + Pb(NO_3)_2 = Pb_2(OH)_2(NO_3)_2 \\ &= 2\,Pb(OH)(NO_3). \\ \text{Basic bismuth nitrate} &= 2\,Bi(OH)_3 + Bi(NO_3)_3 = Bi_3(OH)_6(NO_3)_3 \\ &= 3\,Bi(OH)_2NO_3. \\ \text{Basic lead acetate} &= Pb(OH)_2 + Pb(C_2H_3O_2)_2 = Pb_2(OH)_2(C_2H_3O_2)_2 \\ &= 2\,Pb(OH)(C_2H_3O_2). \\ \text{Bismuth oxychloride} &= Bi_2O_3 + BiCl_3 = Bi_3O_3Cl_3 = 3\,BiOCl. \end{aligned}$$

Basic salts are usually less soluble in water than the corresponding normal salts, but there are exceptions.

90. **Types of Chemical Change.**—In the foregoing chapters we have met with several different kinds of chemical change, and it will be well before going further to classify these under a few main headings.

(1) **Direct combination.**—This consists in the union of two or more simpler molecules (either elementary or compound) to form a more complex molecule. For example, the two elements iron and sulphur combine on heating to form ferrous sulphide; the two compounds quicklime and

water unite to form slaked lime; and the element chlorine unites with the compound carbon monoxide to form phosgene gas—

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Sulphur.}}{S} = \underset{\text{Ferrous sulphide.}}{FeS.}$$

$$\underset{\text{Quicklime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{CaH_2O_2.}$$

$$\underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Phosgene gas}}{COCl_2.}$$

(2) **Simple decomposition.**—This term is applied to the breaking up of a complex molecule into simpler molecules (either elementary or compound). For example, mercuric oxide on heating decomposes into mercury and oxygen, chalk on heating breaks up into quicklime and carbon dioxide, and potassium nitrate on heating yields oxygen and potassium nitrite—

$$\underset{\text{Mercuric oxide.}}{2\,HgO} = \underset{\text{Mercury.}}{2\,Hg} + \underset{\text{Oxygen.}}{O_2.}$$

$$\underset{\text{Chalk.}}{CaCO_3} = \underset{\text{Quicklime.}}{CaO} + \underset{\text{Carbon dioxide.}}{CO_2.}$$

$$\underset{\text{Potassium nitrate.}}{2\,KNO_3} = \underset{\text{Potassium nitrite.}}{2\,KNO_2} + \underset{\text{Oxygen.}}{O_2.}$$

(3) **Simple replacement.**—When an element acts on a compound by replacing another element the change may be termed "simple replacement." Zinc, for example, acts on sulphuric acid and replaces the hydrogen—

$$\begin{tikzcd}
\underset{\text{Zinc.}}{Zn} \arrow[rr, bend right] & + & \underset{\text{Sulphuric acid.}}{H_2SO_4} \arrow[ll, bend right] & = & \underset{\text{Zinc sulphate.}}{ZnSO_4} & + & \underset{\text{Hydrogen.}}{H_2.}
\end{tikzcd}$$

Similarly, iron reacts with copper sulphate and replaces the copper—

$$\begin{tikzcd}
\underset{\text{Iron.}}{Fe} \arrow[rr, bend right] & + & \underset{\text{Copper sulphate.}}{CuSO_4} \arrow[ll, bend right] & = & \underset{\text{Ferrous sulphate.}}{FeSO_4} & + & \underset{\text{Copper.}}{Cu.}
\end{tikzcd}$$

(4) **Double decomposition.**—In this kind of change two compounds react and undergo a mutual exchange of constituents. For example, silver nitrate reacts with sodium chloride to produce silver chloride and sodium nitrate—

$$\begin{tikzcd}
AgNO_3 \arrow[rr, bend left] & + & NaCl \arrow[ll, bend left] & = & NaNO_3 & + & AgCl.
\end{tikzcd}$$

Silver nitrate. Sodium chloride. Sodium nitrate. Silver chloride.

Again, copper oxide and sulphuric acid (or hydrogen sulphate) react to form copper sulphate and water (or hydrogen oxide)—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Water.}}{H_2O.}$$

QUESTIONS.—CHAPTER XII.

1. Write a short history of the term *acid.*
2. Define the terms *acid, salt, base* and *alkali*, and give examples of each class of compounds.
3. What is meant by the *basicity* of an acid? Illustrate your answer by examples.
4. Describe an experiment which proves that sulphuric acid is a dibasic acid.
5. What is the basicity of the following acids:—(1) acetic, (2) phosphoric, (3) hydrochloric?
6. Explain the terms *normal salt* and *acid salt*, and give examples of each class of compounds.
7. What is a *basic salt?* By what methods can basic salts be prepared?
8. State the principal types of chemical change, and give examples of each.

CHAPTER XIII.

COMPOUNDS OF HYDROGEN AND OXYGEN.

91. Hydrogen and oxygen combine together in two proportions, forming water, H_2O, and hydrogen peroxide, H_2O_2; the latter contains twice as much oxygen in relation to hydrogen as the former.

WATER, H_2O.

92. We shall commence the study of water by investigating its composition by volume and by weight.

Composition of Water by Volume.—The composition of water was first proved by Cavendish at the end of the 18th century. He introduced a mixture of two volumes of hydrogen and one of oxygen into a strong glass vessel fitted with two wires which passed into the inside of the vessel so as nearly to touch one another. The electric spark was passed by means of the wires, and the gases exploded. By repeating the experiment many times he was able to show that oxygen combines with twice its volume of hydrogen and that the liquid resulting from the combination was water.

The method employed at the present day to prove the volumetric composition of water is similar in principle to that employed by Cavendish but capable of greater accuracy, and moreover it is applicable to gases in general; it was first introduced by Bunsen.

A tube of even bore, about 70 centimetres in length, is used. This is furnished with platinum wires to enable the gases to be "sparked," and millimetre divisions are etched on the tube. The "eudiometer," as such a tube is called,

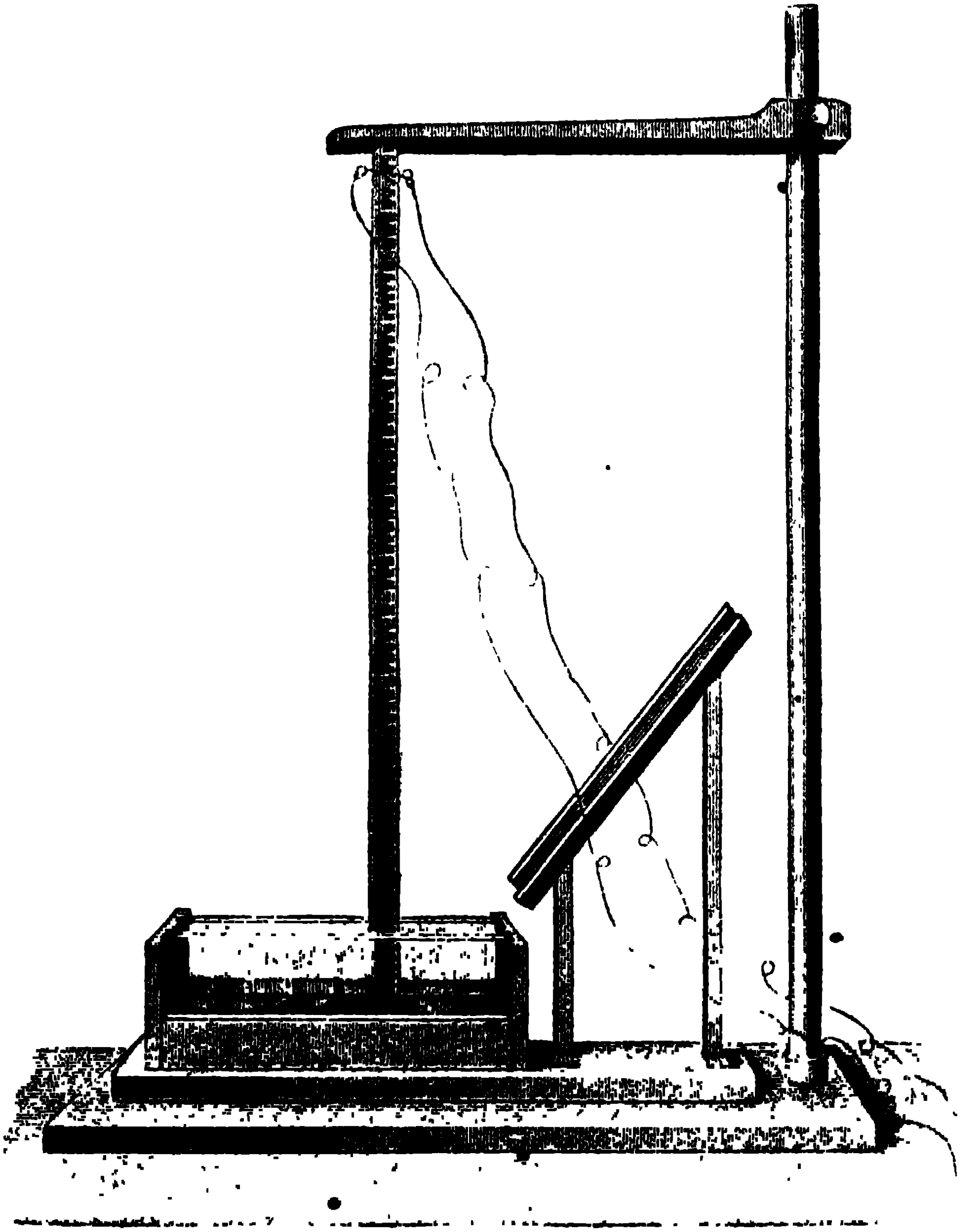

FIG. 29.

is first calibrated so that its relative volume down to any given graduation is known. It is then filled with mercury and inverted in a trough containing mercury (see Fig. 29).

Pure oxygen sufficient to occupy about one-tenth of the volume of the eudiometer is now passed in, and the exact level of the mercury in the eudiometer and in the trough is read. Hydrogen is then added equal to about six or seven times the volume of the oxygen, and the levels of the mercury again read. The temperature and pressure existing at the time must also be noted. The eudiometer is now closed by pressing it down firmly on an india-rubber cushion at the bottom of the trough, and the spark is passed by connecting the platinum wires with a battery and Ruhmkorff coil.

Under these circumstances the whole of the oxygen enters into combination with hydrogen, and as the water which forms condenses a partial vacuum is formed inside the tube, and on gently raising it from the cushion the mercury is seen to rise. After allowing sufficient time for the gas to regain the temperature of the room (much heat having been generated by the combination which has taken place) the levels of the mercury in the eudiometer and trough are again read.

We have now the whole of the data necessary for ascertaining the relative volumes of hydrogen and oxygen which have united to form water. The volumes occupied by the gases are all reduced so as to represent standard conditions. When this has been done, let us suppose—

Oxygen taken	occupied	12	volumes.
Hydrogen added	,,	80	,,
Residual hydrogen	,,	56	,,

It is evident that 12 volumes of oxygen have entered into combination with $80 - 56 = 24$ volumes of hydrogen to form water.

93. Correction for Pressure of aqueous Vapour.—There is one correction in the above description which has been omitted. A small quantity of water vapour is produced on the combination of hydrogen and oxygen, and this vapour exerts a pressure (see § 103), so that the pressure exerted by the residual hydrogen is rather less than that measured as above, which is the total pressure of hydrogen plus water vapour. The amount of water vapour produced is however too small to *saturate* the residual hydrogen, so the vapour pressure cannot be found by reference to the tables referred to in § 103. How then are we to make the necessary correction? The method adopted is to ensure that the residual gas is saturated with aqueous vapour by moistening the eudiometer with a few drops of water before introducing the mercury at the commencement of the experiment. Of course, all the other volumes of gas measured will also be saturated with aqueous vapour, and the pressure which it exerts can be found by noting the temperature of the gas and referring to the tables. If, then, the pressure of any of the volumes of gas as previously measured was found to be P and the saturation pressure of water vapour at the temperature of the gas is p, then the corrected pressure is $P-p$.

The above method of finding the volumetric composition of water is a *synthetic* method. An *analytical* method (electrolysis) has already been described in Chapter III.

94. Volumetric Composition of Steam.—In order to find out the relation between the volumes of hydrogen and oxygen which combine, and that of the steam produced from them, we must so arrange the experiment that the temperature of the gases is maintained above the boiling-point of water. The steam produced will not, under these conditions, condense to water.

The apparatus shown in Fig. 30 may conveniently be used for this experiment. A U-tube, one limb of which is closed and graduated, is fitted with platinum wires for "sparking," as in the Bunsen eudiometer. The tube is filled with mercury. The closed limb is then surrounded by a wider tube through which the vapour of a liquid boiling at about 130° C. (*e.g.* amyl alcohol) is passed.

A mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume (obtained by the electrolysis of water) is now passed into the closed limb by rubber tubing reaching round the bend through the mercury, and the displaced mercury is allowed to run out through the stopcock. When the closed limb is about two-thirds full of gas, the supply is cut off and the rubber tubing removed. The mixture is allowed to attain the temperature of the jacket, the mercury is adjusted to the same level in each limb, and the volume of mixed gases read off. The open end of the tube is closed with a cork (to prevent the explosion from expelling the mercury) and a spark is passed. The gases combine, and on bringing the mercury in each limb to the same level by pouring mercury into the open limb, it will be seen that the volume of steam occupies two-thirds that of the mixed gases. If the tube is now allowed to cool down to the ordinary temperature, the mercury will rise almost to the top of the closed limb—not quite owing to the small vapour pressure which water exerts at ordinary temperature; this shows that there is no hydrogen or oxygen remaining uncombined. From this experiment it follows that steam contains its own volume of hydrogen and half its volume of oxygen, and this agrees with the equation—

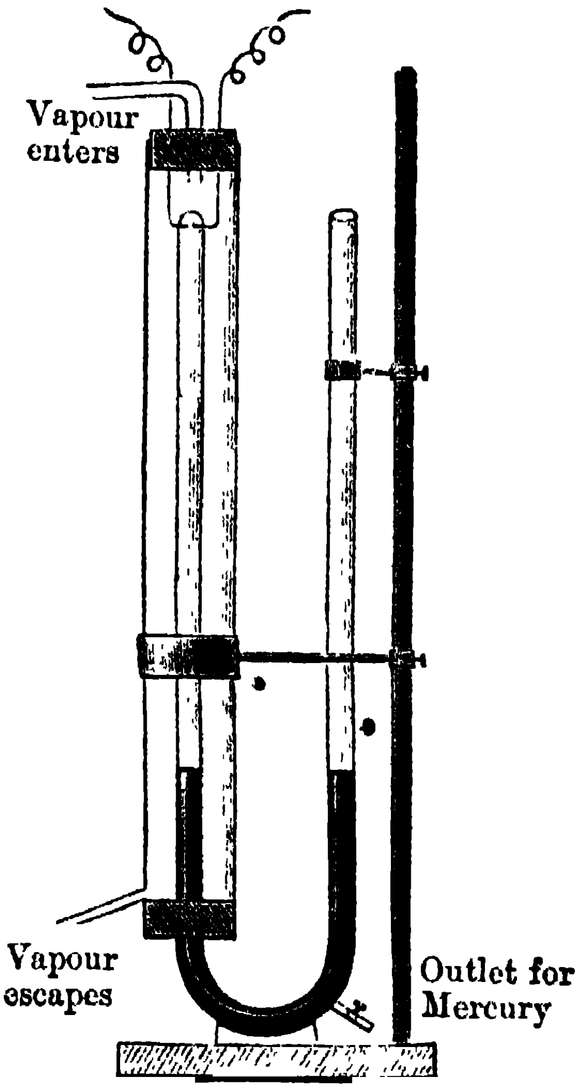

FIG. 30.

$$\begin{array}{ccccc} 2\,H_2 & + & O_2 & = & 2\,H_2O. \\ \text{4 vols.} & & \text{2 vols.} & & \text{4 vols.} \end{array}$$

95. Composition of Water by Weight.—We have seen in Chapter IV. that many oxides, such as those of lead, copper, iron, etc., when heated in a current of hydrogen give up their oxygen, and are "reduced," as it is termed, to the metallic condition. In this reduction the oxygen combines with hydrogen with the production of water. If then we can ascertain (1) the weight of the water formed, and (2) the weight of the oxygen which has gone to form it, we shall have by difference the weight of the hydrogen contained in the water, and thus a full synthesis of water by weight. Very careful experiments have been performed in this way, using oxide of copper (CuO) as the medium for the supply of the oxygen. The equation expressing the reaction is—

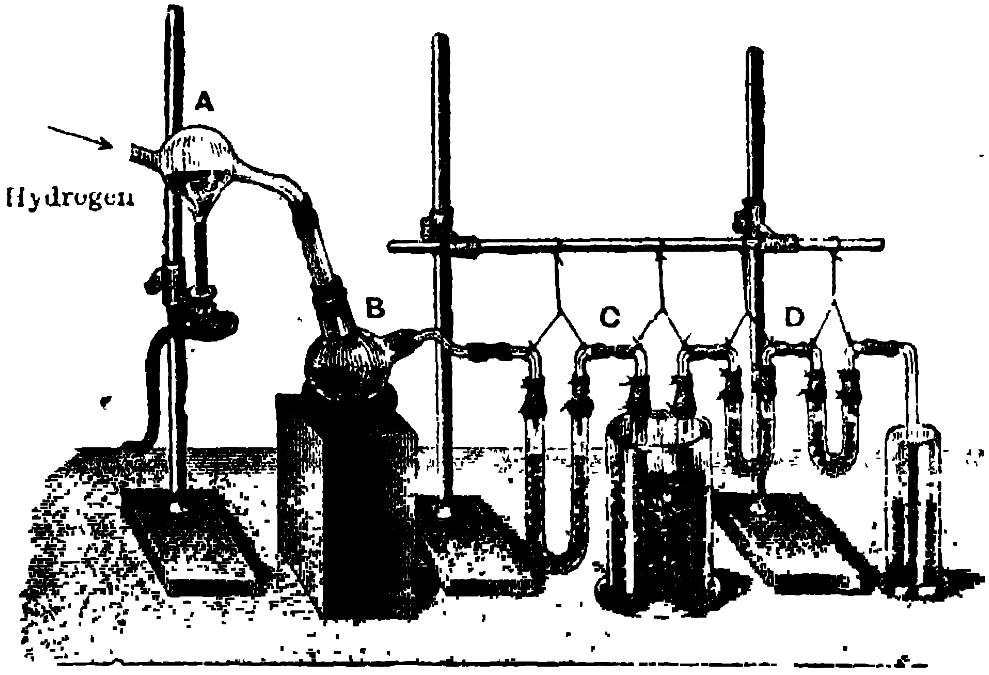

FIG. 31.

$$CuO + H_2 = Cu + H_2O.$$

Our requirements for performing the synthesis are—

(1) Pure hydrogen.

(2) A known weight of oxide of copper.

(3) A means of collecting and weighing the *whole* of the water produced.

Dumas and Stas, in 1843, performed the synthesis of water in this way with extreme care, and the requirements above mentioned were attained in the following manner. The hydrogen, prepared by the action of zinc on sulphuric acid, was purified as described in § 67. The oxide of copper was placed in a bulb A (Fig. 31),* the weight of both being determined. The greater part of the water condensed in the bulb B, and the rest was absorbed in U-tubes containing solid caustic potash C and phosphorus pentoxide D.

Weighings before and after the experiment show—

(*a*) The loss of weight of the oxide of copper, that is the amount of oxygen used;

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* In sketching apparatus the student is advised not to attempt *perspective* drawings which take a long time and are seldom satisfactory. A much better plan is to draw the apparatus *in front elevation*, i. e. as it would be seen by a person looking at it straight in front. When, however, the exact nature of any part of the apparatus can be better explained by drawing it *in section*, i.e. as if it were cut in two through the middle and the front half removed, this method should be adopted for that particular part.

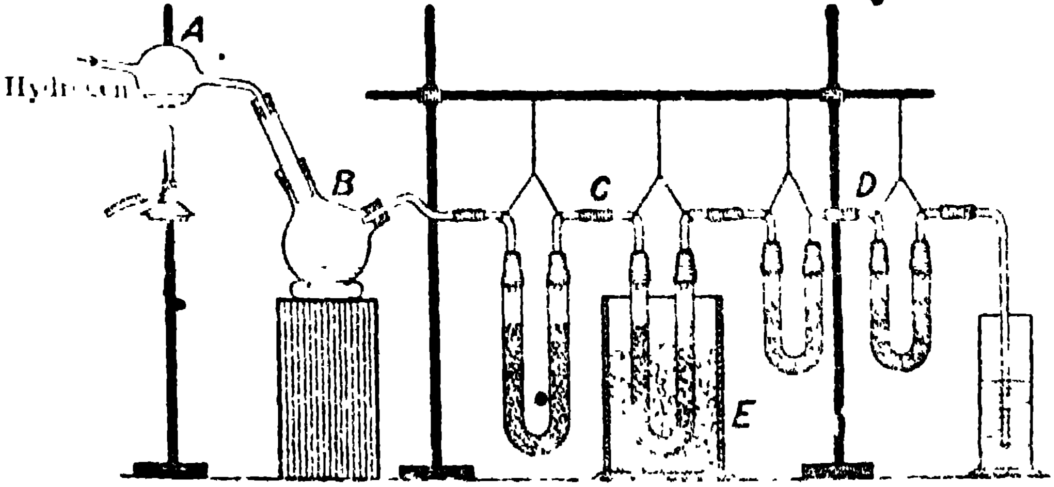

Fig. 32.

To indicate that an object has been cut through, inclined lines are drawn parallel to one another across any part which is sufficiently thick for its two sides to be represented by separate lines (thin glass vessels, for instance, do not admit of this). Fig. 32 is a drawing, partly in front elevation and partly in section, of the apparatus shown in perspective in Fig. 31. For instance, the retort-stands are represented in front elevation in Fig. 32, whilst the vessel B and E are drawn in section.

(*b*) The gain in weight of the second bulb B and the U-tubes succeeding it, that is the amount of water formed. As the combined result of nineteen determinations, they found that the amount of oxygen used was 840·161 grammes and the amount of water formed 945·439 grammes. Water consists, therefore, of

840·161 grammes of oxygen
and 105·278 „ „ hydrogen;

or one part by weight of hydrogen combines with 7·98 parts of oxygen to form water.

More accurate experiments performed in recent years by E. W. Morley and other chemists have shown that the exact ratio by weight in which hydrogen and oxygen combine is 1 : 7·94.

96. **Physical Properties of Water.**—When pure, water is a clear and tasteless liquid; under ordinary circumstances it may be regarded as colourless, but in reality it has a faintly bluish tinge which is perceptible when white light is passed through a stratum of about 20 feet in thickness.

Changes which Water undergoes on the addition and removal of Heat.—These changes are of two kinds—

(1) Change of volume.
(2) Change of state.

Suppose heat is continually abstracted from a given mass of water originally at ordinary temperature (say 15° C.). The temperature gradually falls and the volume gradually diminishes till 4° C. is reached, when the volume ceases to diminish and begins to *increase*, though the temperature continues to fall. A given mass of water has less volume at 4° C. than at any other temperature; 4° C. is therefore the temperature of maximum density of water. At this temperature 1 c.c. of water weighs *exactly* 1 gramme.

When the temperature falls to 0° C. the water gradually becomes solid (*i. e.* it is converted into ice), the volume increasing more rapidly than before. The temperature remains constant at 0° C. till all the water has been converted into ice (though heat is being abstracted all the time), when it again begins to fall. This fall in temperature below 0° C. is accompanied by a slow diminution in the volume of the ice.

Now suppose instead of removing heat from the water at 15° C. we continually add heat to it. This causes a rise of temperature accompanied by increase in volume till 100° C. is reached, when the water gradually changes into the gaseous state (*steam*), with great increase in volume. The temperature does not change till all the water has been converted into steam, when it gradually rises, the volume continuing to increase though much more slowly than during the change from water to steam.

If the preceding processes are reversed, *i.e.* if heat is gradually added to ice below 0° C. or removed from steam at high temperature, all the changes above described take place in the inverse order.

97. The Unit quantity of Heat.—We have seen that the addition of heat to water gradually changes its temperature except when change of state is taking place. It has been found that this change of temperature takes place less rapidly in the case of water than of any other solid or liquid, if heat is supplied at the same rate to equal masses of substances. Water is, therefore, said to have the greatest *capacity for heat* of any liquid. For this reason water is the substance selected in defining the *unit quantity of heat*, which is the *quantity of heat required to raise the temperature of unit mass* (*one gramme*) *of water from* 0° *C. to* 1° *C.* This unit is called the *calorie*.

98. Specific Heat.—The *specific heat* of a substance is the *ratio of the quantity of heat required to raise a given mass of the substance from* 0° *C.* to 1° *C. to that required to raise the same mass of water through the same temperature.* It follows that water has the specific heat 1, and from what has been said above it will be evident that all other solid or liquid substances have a specific heat less than 1. The specific heat of ice is 0·5, and that of steam 0·48.

99. Latent Heat of fusion of Ice.—We noticed that during the change from water into ice heat was continually removed without change of temperature, and that conversely when ice changes into water heat is continually absorbed without change of temperature. The heat so absorbed is said to be *latent* in the water, and the amount absorbed when unit mass (1 gramme) of ice at 0° C. is changed into water at 0° C. is called the *latent heat of fusion of ice.* This quantity may be found by experiment in the following manner:—

Exp. 91.—Weigh out 100 grammes of snow or powdered ice into a thin copper vessel (called a *calorimeter*); support it on corks (cork is a bad conductor of heat), and add 100 grammes of water at 80° C. Stir quickly. The snow will just all melt, and the result will be 200 grammes of water at 0° C.*

To calculate the latent heat of fusion of ice from this result we must equate the heat given out by the water at 80° C. in cooling to water at 0° C., to the heat absorbed by the ice at 0° C. in melting to water at 0° C.; for these two quantities are necessarily equal.

Let x = Latent heat of fusion of ice.

Then—

Heat given out by 100 grammes of water in cooling from 80° C. to 0° C. = 100 × 80 calories.

Heat absorbed by 100 grammes of ice at 0° C. on being converted into water at 0° C. = 100 × x calories.

$$\therefore 100 \times 80 = 100 \times x$$
$$x = 80 \text{ calories,}$$

i. e. the latent heat of fusion of ice is 80 calories.

100. Latent Heat of vaporisation of Water.—Just as heat is rendered latent when ice changes to water, so it is rendered latent when water changes to steam. *The amount of heat absorbed in changing unit mass (one gramme) of water at* 100° *C. into steam at* 100° *C.* is termed the *latent*

---

* In practice the final temperature when all the ice is melted may not be exactly 0° C. owing to various sources of error.

heat of vaporisation of water. Its value has been found by experiment to be 536 calories.*

Latent Heat of substances other than Water.—This property of absorption or evolution of heat without change of temperature during change of physical condition is not peculiar to water, but is quite a general property of substances.

For example, a few drops of ether placed on the hand quickly evaporate and give rise to sensation of intense cold; the explanation is that the heat required to vaporise the ether (*i. e.* its latent heat of vaporisation) is abstracted from the nearest object, *i. e.* the hand.

101. **Freezing Mixtures.**—Many salts, such as ammonium nitrate, potassium iodide, and calcium chloride, on dissolving in water produce a considerable fall of temperature. This is due to the change of state of the salt from solid to liquid, the heat required for this change (*i. e.* the latent heat of fusion) being absorbed from the water. The freezing mixture most commonly employed, however, is a mixture of common salt and snow or powdered ice. On mixing *both* these substances melt and absorb their latent heat of fusion from the mixture, the temperature of which falls to – 23° C.

102. **Evaporation of Water at ordinary temperature.**—We have seen that at 100° C. water boils and is converted into vapour. Water, however, gradually evaporates at ordinary temperature, and even ice very slowly passes away as vapour.

Exp. 92.—Leave a little water in a dish for a day or two, and note its gradual disappearance.

103. **Pressure of Aqueous Vapour.**—It can easily be demonstrated by experiment that water vapour exerts a pressure even at ordinary temperature.

Exp. 93.—Take a eudiometer tube about 85 centimetres long, fill it with mercury, and invert in a trough of mercury.

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* For details of the method the student is referred to standard works on Physics.

The level of the mercury will fall a little, leaving a vacuum at the top of the tube. Introduce a *few* drops of water into the vacuous space by means of a curved pipette; notice that it rapidly vaporises causing depression of the mercury This shows that water vapour exerts a pressure, the amount of which is measured by the depression of the mercury. Now introduce a few more drops of water. This will probably vaporise and produce a further depression of the mercury, but a point will soon be reached when no more water evaporates and no further depression takes place. The space above the mercury is then said to be *saturated* with water vapour, and if any more water is introduced it merely rests upon the surface of the mercury. If the temperature is raised the space becomes unsaturated again and more water will evaporate, producing a further depression of the mercury. This goes on till the space becomes saturated at the higher temperature, when the depression ceases. For each particular temperature the pressure of *saturated* aqueous vapour has a particular value, which is called the *maximum* or *saturation pressure* of aqueous vapour for that temperature. This saturation pressure is the same whether another gas, *e. g.* air, is present or not.

Tables have been constructed for reference, which give the maximum pressure of aqueous vapour at different temperatures.

104. The boiling-point of Water.—Now consider what happens when water is gradually heated in an open vessel. Evaporation takes place at all temperatures, but more rapidly as the temperature rises, because the saturation pressure increases rapidly with increase of temperature. Finally the liquid boils, *i. e.* bubbles form in its interior, rise to the surface, and burst. This, however, cannot take place till the saturation pressure of aqueous vapour is equal to (or, strictly speaking, slightly greater than) the pressure of the atmosphere; before this is the case a bubble would immediately be squeezed up if it were formed, owing to its inability to withstand the external pressure exerted on it. The boiling-point of water may therefore be defined as *the temperature at which its maximum vapour pressure is equal to the atmospheric pressure.* It follows that the boiling-point of water changes when the atmospheric pressure changes.

By substituting the word *liquid* for *water* the above definition becomes quite general.

105. **Water as a Solvent.**—Most of the solid substances and gases which we meet with in chemical operations dissolve to an appreciable extent in water; some liquids, such as alcohol and sulphuric acid, associate themselves with water in all proportions; whilst others, such as oils, if shaken up with water separate again, being taken up by the water either only to a slight extent or not at all.

106. **Solubility of Solids.**—The extent to which solid substances are soluble in water under similar circumstances varies according to the nature of the substance.

Minerals, such as coal, limestone, quartz, and some chemical compounds, such as sulphate of lime, oxide of lead, sulphide of iron, are only very slightly soluble, whilst others, *e.g.* nearly all chlorides and nitrates, are freely soluble. In any case, however, there is a limit to the amount of solid matter which can be dissolved, and when water has taken up as much as it will, we have what is known as a *saturated* solution.

The quantity of a substance required to form a saturated solution is usually greater the higher the temperature, though there is no simple general relation between the temperature and the amount dissolved.

The solubility in parts per 100 of water is given for a few substances in the following table—

	0° C.	20° C.	50° C.	100° C.
Potassium nitrate ...	13·3	31·2	85·0	246·0
Sodium chloride ...	35·5	36·0	37·0	39·6
Potassium chlorate ...	3·3	8·0	19·0	58·0
Sodium chlorate ...	81·9	99·0	136·0	232·6
Mercuric chloride ...	5·7	7·4	11·3	54·0
Potassium sulphate ...	8·3	12·5	17·0	26·0

107. **Solubility of Gases.**—There is no general connection between the solubility of gases and their chemical composition. The very soluble gases are all, however, acid or alkaline in presence of water. Some gases, such as nitrogen, hydrogen, and carbon monoxide, are very slightly soluble, whilst others, such as ammonia, sulphur dioxide, and hydrochloric acid, are very freely soluble in water. The solubility, instead of increasing with the temperature, as in the case of solids, *decreases*, though in no simple relation. One volume of water at the temperatures stated, and under 760 mm. pressure, dissolves the volumes of the respective gases given in the following table—

	0° C.	10° C	20° C.
Nitrogen	0·020	0·016	0·014
Oxygen	0·041	0·033	0·028
Hydrogen	0·019	0·019	0·019
Carbon dioxide	1·799	1·185	0·901
Sulphuretted hydrogen ...	4·371	3·586	2·905

As instances of much more soluble gases we may take—

Sulphur dioxide	79·8	56·6	39·4
Hydrochloric acid	503·0	475·0	444·0
Ammonia	1049·6	812·8	654·0

108. **The influence of Pressure on the solubility of Gases.**—*The weight of a given gas which dissolves in unit volume of a given liquid is directly proportional to the pressure of the gas.* This relation was discovered by Henry, and is known as *Henry's Law*.

Thus 1 c.c. of water at 0° C. dissolves the following weights of carbon dioxide—

At	1 atmosphere	pressure	0·0356	gm.
,,	2 atmospheres	,,	0·0713	,,
,,	4 ,,	,,	0·1426	,,
,,	$\frac{1}{2}$ atmosphere	,,	0·0178	,,
,,	$\frac{1}{3}$,,	,,	0·0119	,,

Soda-water is water charged with carbon dioxide under a pressure of about 4 atmospheres, and so long as this pressure on the surface of the water is maintained this volume of gas will be retained, but directly the pressure is released an effervescence is observed, and gas escapes from the liquid in proportion to the diminution of pressure.

109. **Solution of Mixed Gases.**—At 0° C. and standard pressure a litre of water will dissolve 41 c.c. of oxygen. If, however, we mix another gas, say nitrogen, with the oxygen, a smaller volume of oxygen (reduced to standard pressure) will be found to dissolve a volume indeed proportional to the pressure of the oxygen alone (Dalton's Law of Partial Pressures). In the same way the nitrogen will no longer dissolve to the extent of 20 c.c. (see table), but to a smaller extent, in proportion to the pressure due to the nitrogen alone. For mixed gases, therefore, solution takes place in accordance with (*a*) the solubility of the gas in question, (*b*) the pressure exerted by it independently of any other gas or gases that may be present in the mixture.

Let us consider the important case of the solution of air (taken as 79 volumes of nitrogen[*] and 21 of oxygen) in water—

The oxygen dissolved by a litre of water from air will, according to this law, be, not 41 c.c., but

$$\frac{41 \times 21}{100}, \text{ or } 8{\cdot}6 \text{ c.c. per litre.}$$

The nitrogen dissolved will be, not 20 c.c., but

$$\frac{20 \times 79}{100}, \text{ or } 15{\cdot}8 \text{ c.c. per litre.}$$

So that in consequence of its greater solubility the proportion of oxygen to nitrogen dissolved in water is 8·6 : 15·8, and is therefore 35 per cent. of the whole. Air expelled from solution in water by boiling or by exposure to a vacuum is, then, much richer in oxygen than ordinary air.

So taking 0·04 as the normal percentage of carbon dioxide in air, this gas will be dissolved, not to the extent of 1,799 c.c. to the litre, but

---

[*] Argon is here reckoned as nitrogen.

$$\frac{1{,}799 \times 0{\cdot}04}{100}, \text{ or } 0{\cdot}72 \text{ c.c. per litre.}$$

Now 1 litre of water dissolves $8{\cdot}6 + 15{\cdot}8 + 0{\cdot}72 = 25{\cdot}12$ c.c. of oxygen + nitrogen + carbon dioxide from the air. Of this carbon dioxide constitutes $\frac{0{\cdot}72}{25{\cdot}12} \times 100 = 2{\cdot}87$ per cent. Air dissolved in water is, therefore, $\frac{2{\cdot}87}{0{\cdot}04} = 71\frac{3}{4}$ times as rich in carbon dioxide as the original air taken.

110. **Natural Waters.**—The water which evaporates from the surface of sea and land, and passes as water vapour into the air, is the purest form of natural water, and it retains its purity until it begins to fall as drops from the rain cloud.

Rain Water.—When this is collected at the surface of the earth it has passed through a considerable stratum of air, and dissolved in its passage not only gases normally occurring in the atmosphere, but also such impurities as are found there. Even then the solid matter contained in it does not amount normally to more than 3 or 4 parts per 100,000. In the neighbourhood of towns the impurities taken up are more numerous and in larger quantity; also near the sea, and especially during high winds, much sodium chloride is found in rain water.

River Water.—The composition of this water will of course depend on the nature of the surface and of the strata over which the water passes. For instance, a considerable part of the drainage area of the Thames consists of chalk, and its water contains about 30 parts of dissolved matter in 100,000, two-thirds of this consisting of calcium carbonate and sulphate, whilst the Dee in Scotland, passing over the older strata (principally slate and sandstone), contains about 5·6 parts of dissolved matter per 100,000, one-fourth of this being calcium salts. Since the water which passes into rivers collects from the surface of the soil, it contains also much more organic matter and carbon dioxide than rain water, arising from contact with plants and decaying vegetable matter.

Spring Water.—The water of springs is rain water which has percolated through soil and rocks. The composition of spring waters varies very considerably according to the depth from which the water rises and the nature of the strata which it has traversed. In some cases the amount of dissolved matter is very large, and such springs; especially when they have a saline taste or medical properties, are known as *mineral* springs.

The springs of Bath and Harrogate contain magnesia and sulphuretted hydrogen, and are known as magnesia and sulphur waters; a spring near Woodhall Spa contains free iodine; many springs contain iron, and are known as *chalybeate* waters.

Mineral springs which rise from great depths are frequently hot, some having a temperature of nearly 100° C.; this is especially the case in volcanic regions, where the earth's temperature rises more rapidly with increase in depth below the surface than elsewhere.

Spring water is bright and sparkling, since it is more fully charged with gases than either rain or river water, and contains less organic matter, this being removed in its passage through beds of soil or gravel. The composition of some typical waters is given in the table further down.

Sea Water.—The matters dissolved or suspended in river or spring water are carried to the sea and remain there, since the water vapour rising from the sea consists of practically pure water; so that, notwithstanding the removal of large quantities of these substances by settling out or by the action of organisms, sea water is very impure. The water from the open ocean contains on the average about 3·5 per cent. of dissolved solids and has a specific gravity of about 1·03; the greater part of this soluble matter, nearly four-fifths, consists of sodium chloride, the remainder being chiefly calcium and magnesium sulphates and calcium chloride. The peculiar taste of sea water is due to the presence of these salts. There are, however, certain land-locked seas where the evaporation is very rapid and the quantity of dissolved solids is much greater than in sea-water; the Dead Sea, for example, contains nearly 23 per cent. of impurities.

In the following table details are given of the composition of some typical natural waters, the solids in parts per 100,000, the gases in cubic centimetres per litre:—

COMPOSITION OF SOME NATURAL WATERS.

	Solids.					Gases.		
	Total Residue.	Calcium Salts.	Magnesium Salts.	Sodium Chloride.	Organic Matter.	N.	O.	CO_2.
Rain Water	3·4	*nil*	*nil.*	0·5	1·0	13·1	6·4	1·8
River Water (Thames)	29	20	1·8	2·6	3·4	15·0	7·4	30·3
River Water (Dee)	5·6	1·4	0·5	1·0	2·2			
Spring Water	20			2·0	Traces	15·8	8·6	1·0
Mineral Water (Bath)	236	137	23	34	Traces	4·0	2·0	29·0
Sea Water	3,500	140	530	2,650	Traces	12·1	6·0	17·0

Chemically pure water may be obtained by distillation, the water being boiled and the steam which is given off condensed. On a small scale the apparatus shown in Fig. 9, § 20, may be used. The water is boiled in a flask connected with a condenser, through which a continual stream of cold water passes for the purpose of condensing the steam.

A small quantity of volatile organic matter may be carried over during a first distillation, and soluble matter from the glass condenser and receiver may be present; but on adding a few drops of potassium permanganate solution, and distilling again in platinum apparatus, very pure water is obtained.

111. Drinking Water.—When water is to be used for drinking purposes, it is of the highest importance that it should be clear and colourless, and as free as possible from organic impurity arising from sewage contamination or contact with decaying animal or vegetable matter. Dissolved salts, such as ordinarily occur in natural waters, are of less moment than organic impurity, and even such minute quantities of the latter as 0·3 or 0·4 parts per 100,000 may be injurious. The taste of drinking water is also an important factor, and whilst distilled water and rain water are flat and insipid owing to the smaller quantity of dissolved gases which they contain, spring water has a characteristic freshness which renders it most palatable.

112. **Hardness of Water.**—It is a matter of common experience that the sensation felt when washing the hands differs with waters from different sources. With rain water or the waters derived from sandstone areas a lather quickly forms, whilst with calcareous waters there is a sense of harshness and a good deal of soap is required to produce a lather; we notice further that in the latter case a scum is formed which floats on the surface of the water. Waters that readily form a lather are known as *soft* waters, whilst those which do not are called *hard* waters. Hard waters contain much dissolved matter, and especially bicarbonates and sulphates of calcium and magnesium and chlorides of sodium and magnesium, which are the chief causes of the hardness. Soap consists of the sodium or potassium salts of certain complex acids composed of carbon, hydrogen and oxygen (called *fatty acids*). These salts are soluble in water, and the solution possesses the remarkable property of preventing finely-divided particles of fats from running together in it. Such an intimate mixture of fat particles and water is termed an *emulsion*, and the cleansing properties of soap are due to the formation of an emulsion of any particles of grease by the action of the soapy water. Now the calcium and magnesium salts of the fatty acids present in soap are *insoluble* in water, so that on adding soap to water containing salts of these metals in solution, double decomposition immediately takes place between the soap and the salts with precipitation of the insoluble calcium and magnesium salts of the fatty acids. It is these insoluble salts which form the scum already referred to, and no soap is available for cleansing purposes till all the calcium and magnesium have been removed from the solution by precipitation.

The hardness produced by a solution of sodium chloride is due to a different cause, namely, the insolubility of soap in it.

Exp. 94.—Prepare a solution of soap by dissolving a few grammes of soap in about 200 c.c. of distilled water. Add some of this solution separately to solutions of calcium sulphate, magnesium sulphate and chloride, and sodium chloride (the last should be strong); note the flocks of insoluble calcium and magnesium salts formed in the first three cases and the curds of insoluble soap in the last.

Exp. 95.—Suspend some chalk in water and pass in carbon dioxide; when the solution is saturated filter it. Shake also some chalk with water and filter. Test the two solutions by soap solution: that through which the carbon dioxide has passed is very hard; the other is soft.

The explanation of this is that chalk (calcium carbonate) is insoluble in pure water, but dissolves in water containing carbon dioxide, with formation of acid calcium carbonate or calcium bicarbonate, $Ca(HCO_3)_2$.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

The bicarbonate reacts with soap just like any other soluble calcium salt. Magnesium bicarbonate $Mg(HCO_3)_2$ may be formed from magnesia alba (basic magnesium carbonate) in a similar manner.

113. Temporary Hardness and its Removal.

Exp. 96.—Boil some of the calcium bicarbonate solution obtained in the last experiment for a few minutes. A precipitate is formed; allow this to settle, pour off the clear liquid and add soap solution to it. No precipitate is formed, showing that the hardness has been removed.

What has happened is that on boiling the calcium bicarbonate was decomposed into normal calcium carbonate, water and carbon dioxide.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The carbon dioxide passed away as a gas and the calcium carbonate was precipitated.

The "fur" which forms on a steam boiler and on a kettle is chiefly calcium carbonate produced during the process of boiling.

Magnesium bicarbonate undergoes a similar decomposition on boiling, and these two bicarbonates are the chief causes of what is known as *temporary hardness*, i. e. hardness which can be removed by boiling.

There is another way in which temporary hardness can be removed, viz. by the addition of lime; this decomposes the bicarbonates with precipitation of normal carbonates. Calcium bicarbonate, for example, is decomposed in the following manner :—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O.$$

This is known as Clark's process.

114. **Permanent Hardness and its Removal.**—The hardness due to salts other than bicarbonates cannot be removed by boiling, and is called *permanent* hardness.

When permanent hardness is due to salts of magnesium and calcium it can be removed by the addition of washing soda ($Na_2CO_3 + 10\ H_2O$), which precipitates the magnesium and calcium as insoluble carbonates :—

$$\underset{\text{Calcium sulphate.}}{CaSO_4} + Na_2CO_3 = \underset{\text{ppt.}}{CaCO_3} + Na_2SO_4$$

$$\underset{\text{Magnesium chloride.}}{MgCl_2} + Na_2CO_3 = \underset{\text{ppt.}}{MgCO_3} + 2\ NaCl.$$

Washing soda also removes *temporary* hardness. Magnesium bicarbonate, for instance, is decomposed in the following manner :—

$$Mg(HCO_3)_2 + Na_2CO_3 = 2\ NaHCO_3 + \underset{\text{ppt.}}{MgCO_3}.$$

Hardness due to sodium chloride, being caused by the insolubility of soap in the solution, cannot of course be removed by the addition of washing soda. There are, however, certain soaps which are soluble in brine such as *marine soap*, and these enable us to get over the difficulty.

All kinds of hardness can of course be removed by distillation.

115. **Estimation of Hardness.**—The hardness of a sample of water is determined by finding how much of a standard soap solution is required to produce a permanent lather with a known volume of the water. This gives the *total*

hardness, *i. e.* the temporary and permanent hardness combined. The *permanent* hardness is found by boiling a known volume of the water for a short time to remove temporary hardness and then adding standard soap solution as before. The difference between the total and permanent hardness gives the *temporary* hardness.

Let us compare the hardnesses of various kinds of waters by performing the following experiment :—

Exp. 97.—Weigh out 10 gms. of sodium oleate or green Castile soap and dissolve it in 1 litre of water. If you wish the solution to keep, it is better to use 650 c.c. of water and 350 c.c. of methylated spirit: this is your standard soap solution. Measure 50 c.c. each of distilled water, rain water, well water, and sea water into 6-oz. bottles, and run the soap solution from a burette or measuring-tube into each until a lather is formed by shaking, which does not break for five minutes. Note the volume of soap solution required for each. Evaporate 20 c.c. of each water and compare the residues in each case: the water which requires most soap for a permanent lather leaves the largest residue.

It will be found that the order of hardness is (1) sea water, (2) well water, (3) rain water and distilled water (practically equal).

116. Chemical Properties of Water.—Water possesses the power of combining directly with a very great many substances. Sometimes the compounds are very easily broken up again, whilst in other cases they are remarkably stable.

Water of Crystallisation.—Many salts, when they are allowed to crystallise from solution, contain water, which is associated with them in definite proportions, and it cannot be regarded otherwise than as water *in combination* with the salt.

There is, however, very little stability in the combination; for instance, copper sulphate crystallises with the composition $CuSO_4 + 5\,H_2O$. At 100° C. $4\,H_2O$ is set free, and the remaining molecule of water requires a temperature of 240° C. to liberate it.

Alum crystallises with 24 H_2O; 10 H_2O separate at 100° C., a further 9 H_2O at 120° C., and nearly the whole of the remainder at 280° C. In some cases, indeed, such as crystallised sodium carbonate or washing soda, $Na_2CO_3 + 10\ H_2O$, the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.

The amount of water of crystallisation which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of $Na_2SO_4 + 7\ H_2O$ can be obtained at temperatures below 26°, or crystals of $Na_2SO_4 + 10\ H_2O$ (Glauber's salt) at temperatures below 34°; while above 34° crystals of Na_2SO_4 are obtained. Epsom salts, $MgSO_4 + 7\ H_2O$, furnishes another example, giving $MgSO_4 + 6\ H_2O$. Frequently, salts which at ordinary temperatures separate from solution in the anhydrous condition, possess water of crystallisation when crystallised at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of NaCl are obtained, but at - 10° C. crystals of $NaCl + 2\ H_2O$.

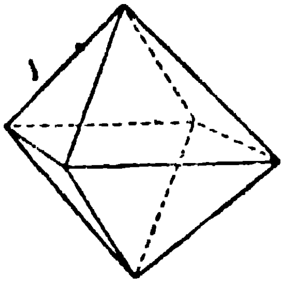

Alum.
$K_2SO_4 . Al_2(SO_4)_3 . 24\ H_2O$.

FIG. 33.

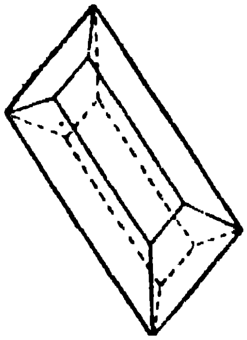

Washing soda.
$Na_2CO_3 . 10\ H_2O$.

FIG. 34.

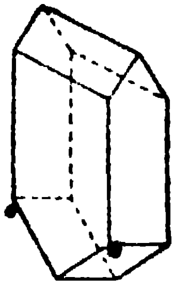

Epsom salts.
$MgSO_4 . 7\ H_2O$.

FIG. 35.

As examples of the crystalline forms assumed by salts containing water of crystallisation, we may consider three very common substances, viz. alum, washing soda, and Epsom salts. Figs. 33, 34 and 35 represent crystals of these substances, and it will be noticed how widely the three crystals differ in shape.

117. Compounds of Water with Oxides.—We have seen in discussing acids and bases that many oxides combine directly with water. The products vary in stability, but are as a whole very much more stable than those obtained when salts and water combine.

In many cases great heat is evolved when oxides and water unite, thus demonstrating the vigorous nature of the action.

Exp. 98.—Pour a *little* water on to some quicklime contained in a porcelain dish. Note the clouds of steam formed, showing that much heat is evolved during the combination. Dip a thermometer in the mixture and note the rise of temperature.

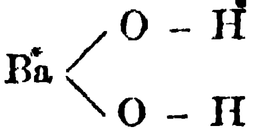
Other examples of oxides which evolve much heat on combination with water are BaO, SO_3, P_2O_5. To bring about the decomposition of the compounds produced a correspondingly large amount of heat must be supplied, *i. e.* a high temperature is necessary.

To explain the greater stability of the compounds of water with oxides as compared with the compounds with salts, it is supposed that in the latter the water is present in *whole molecules* loosely combined with the molecule of the salt, whereas in the former it has completely lost its identity. Thus crystallised copper sulphate may be formulated $CuSO_4 + 5\,H_2O$ or $CuSO_4 \cdot 5\,H_2O$, but barium hydroxide must not be represented $BaO + H_2O$ or $BaO \cdot H_2O$, *i. e.* as containing a molecule of BaO and a molecule of water; it must be written $Ba(OH)_2$, *i. e.* it contains two *hydroxyl* (OH) groups united to an atom of barium.

The constitutional formulæ, adopting the two methods, will bring out the difference clearly

(1) $\mathrm{Ba = O + H - O - H}$

(2)



$$\mathrm{Ba}\left\langle \begin{matrix} \mathrm{O - H} \\ \mathrm{O - H} \end{matrix} \right.$$

It is supposed that all the compounds of water with oxides contain one or more (OH) groups, and they are consequently called *hydroxides*, whereas the combinations of salts and water are termed *hydrates*.

Action of Metals on Water.—This has been fully discussed in § 27, and does not require further treatment here.

118. **Action of Water on Compounds containing Chlorine.**—Many compounds of non-metals with chlorine or chlorine and oxygen react vigorously with water producing hydrochloric acid and another acid (or sometimes an oxychloride). Such substances are phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, phosphorus oxychloride, $POCl_3$, and sulphuryl dichloride, SO_2Cl_2. The phosphorus compounds react with water according to the following equations:—

$$PCl_3 + 3\,H_2O = \underset{\text{Phosphorous acid.}}{H_3PO_3} + 3\,HCl.$$

$$PCl_5 + H_2O = POCl_3 + 2\,HCl \text{ (with a little water).}$$

$$POCl_3 + 3\,H_2O = \underset{\text{Phosphoric acid.}}{H_3PO_4} + 3\,HCl \text{ (with more water).}$$

On combining the last two equations to represent the reaction of PCl_5 with excess of water we get—

$$PCl_5 + 4\,H_2O = H_3PO_4 + 5\,HCl.$$

The reaction between sulphuryl dichloride and water is represented thus—

$$SO_2Cl_2 + 2\,H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4} + 2\,HCl.$$

119. **Tests for Water.**—To distinguish water from other colourless liquids the following tests may be applied:—

(1) Add a few drops of the liquid to a small quantity of anhydrous copper sulphate (prepared by igniting some powdered blue vitriol in a crucible till it is perfectly white and allowing it to cool in a desiccator). Water rehydrates it and changes the colour from white to blue.

(2) Add a little of the liquid to some quicklime (see Exp. 98).

(3) Drop a small pellet of sodium or potassium (about the size of a pea) on to a portion of the liquid. If the liquid is

water hydrogen will be evolved and will take fire in the case of potassium.

To decide whether water is *pure* or not its physical properties may be utilised. The liquid should

(*a*) be colourless, tasteless and odourless;
(*b*) freeze at 0° C.;
(*c*) boil at 100° C. under 760 mm. pressure.

Moreover, pure water should give no precipitate or coloration with (1) *silver nitrate* (showing absence of chlorides, (2) *barium chloride* (showing absence of sulphates), (3) *Nessler's solution* (showing absence of ammonia), (4) *lime water* (showing absence of carbonates).

HYDROGEN PEROXIDE, H_2O_2.

120. This substance has been found in very small quantities in rain and snow, and also in the water formed by the combustion of hydrogen.

It is produced in small quantity during the slow oxidation of phosphorus and in larger quantities when turpentine is shaken with water in the presence of air.

Preparation.—The peroxides of the alkali and alkaline earth metals yield hydrogen peroxide on treatment with dilute acids. Either barium peroxide or sodium peroxide is generally used in practice. The following are the details of the preparation of the pure substance using barium peroxide and sulphuric acid:—

Some dilute sulphuric acid is placed in a beaker and surrounded by a freezing mixture of ice and salt to keep its temperature low. A cream of barium peroxide and water which has also been cooled in a freezing mixture is then slowly run into the acid with constant stirring. Barium sulphate is precipitated and hydrogen peroxide goes into solution. Excess of barium peroxide must not be added or it will decompose the hydrogen peroxide. The best way is to add rather less than an equivalent quantity of barium peroxide (*i. e.* keep the solution acid to test paper) and remove the excess of acid by barium carbonate. The barium sulphate and any excess of barium carbonate are filtered off, and the filtrate evaporated on the water-bath, the temperature not being allowed to rise above 75° C., or the hydrogen peroxide will be decomposed. By this means a considerable part of the water is driven off. The final purification is accomplished by fractionally distilling the liquid under reduced pressure (about 10 mm. of mercury). Water comes off first, and when this has all been removed the receiver is changed; on continuing the distillation hydrogen peroxide passes over in an almost pure state.

The equation representing the formation of hydrogen peroxide from barium peroxide and sulphuric acid is—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

121. **Properties.**—Hydrogen peroxide is a thick liquid with a specific gravity about 1·5; it is colourless in small masses, but in large masses it has a decidedly bluer colour than water.

Hydrogen peroxide is remarkable for the ease with which it breaks up into water and oxygen according to the equation—

$$2\,H_2O_2 = 2\,H_2O + O_2.$$

The pure substance decomposes with explosive violence on slight rise of temperature, and the dilute aqueous solution loses oxygen rapidly on boiling.

Hydrogen peroxide affords another interesting example of catalysis, for its dilute solution decomposes rapidly at ordinary temperature in contact with certain metals such as finely-divided platinum, the latter undergoing no change.

122. **Oxidising Action of Hydrogen Peroxide.**—Owing to the ease with which hydrogen peroxide parts with an atom of oxygen it is a powerful oxidising agent. Thus it converts lead sulphide into lead sulphate, according to the equation—

$$\underset{\text{Lead sulphide.}}{PbS} + 4\,H_2O_2 = \underset{\text{Lead sulphate.}}{PbSO_4} + 4\,H_2O.$$

Ordinary molecular oxygen will not bring about this change except on heating. We have, however, seen in discussing ozone that atomic oxygen is more active than molecular oxygen, and it is the atomic oxygen produced when hydrogen peroxide decomposes which acts so readily on the lead sulphide. We may therefore represent the reaction in two stages—

$$4\ H_2O_2 = 4\ H_2O + \underset{\text{Atomic.}}{4\ O.}$$

$$PbS + \underset{\text{Atomic.}}{4\ O} = PbSO_4.$$

This reaction is made use of in restoring the colour of old pictures which have been blackened by the action of sulphuretted hydrogen on the lead paint. The hydrogen peroxide converts the *black* lead sulphide into *white* lead sulphate. Other examples of its oxidising action are represented in the following equations:—

$$\underset{\text{Sulphuretted hydrogen.}}{H_2S} + H_2O_2 = 2\ H_2O + \underset{\text{Sulphur.}}{S.}$$

$$\underset{\text{Calcium monoxide.}}{CaO} + H_2O_2 = \underset{\text{Calcium dioxide.}}{CaO_2} + H_2O.$$

$$\underset{\text{Potassium iodide.}}{2\ KI} + H_2O_2 = \underset{\text{Caustic potash.}}{2\ KOH} + \underset{\text{Iodine.}}{I_2.}$$

Hydrogen peroxide possesses the power of bleaching many vegetable and animal colours, and is much used for bleaching hair, silk, ivory, etc. It also destroys decaying organic matter, and consequently finds application as a disinfectant. Both these properties depend upon its oxidising action.

123. **Reducing action of Hydrogen Peroxide.**—When silver oxide, Ag_2O, is treated with hydrogen peroxide a mutual decomposition takes place; the silver oxide is reduced to silver and the hydrogen peroxide to water, and a molecule of oxygen is evolved—

$$Ag_2O + H_2O_2 = 2\ Ag + H_2O + O_2.$$

The explanation of this is that both silver oxide and hydrogen peroxide contain a loosely-combined atom of oxygen, and the attraction of these two atoms for one another is greater than their respective attractions for silver and water. They consequently break away and unite to form a molecule of oxygen. We may represent this in the following way, a thick arrow indicating greater attracting force than a thin arrow—

$$\mathrm{Ag_2} \overset{\vdots}{\underset{\vdots}{\leftarrow}} \mathrm{O} \boldsymbol{\rightarrow}\boldsymbol{\leftarrow} \mathrm{O} \overset{\vdots}{\underset{\vdots}{\rightarrow}} \mathrm{OH_2}.$$

Other examples of the reducing action of hydrogen peroxide explained in a similar manner are represented by the following equations:—

$$\underset{\text{Manganese dioxide.}}{\mathrm{MnO_2}} + \mathrm{H_2O_2} = \underset{\text{Manganous oxide.}}{\mathrm{MnO}} + \mathrm{H_2O} + \mathrm{O_2}.$$

$$\underset{\text{Chromium trioxide.}}{2\,\mathrm{CrO_3}} + 3\,\mathrm{H_2O_2} = \underset{\text{Chromic oxide.}}{\mathrm{Cr_2O_3}} + 3\,\mathrm{H_2O} + 3\,\mathrm{O_2}.$$

$$\mathrm{H_2O_2} + \underset{\text{Ozone.}}{\mathrm{O_3}} = \mathrm{H_2O} + 2\,\mathrm{O_2}.$$

Potassium permanganate in acid solution is also reduced—

$$2\,\mathrm{KMnO_4} + 4\,\mathrm{H_2SO_4} + 5\,\mathrm{H_2O_2} = 2\,\mathrm{KHSO_4} + 2\,\mathrm{MnSO_4} + 8\,\mathrm{H_2O} + 5\,\mathrm{O_2}.$$

124. Experiments with Hydrogen Peroxide.—To illustrate the preparation and properties of hydrogen peroxide, the following course of procedure may be adopted:—

Exp. 99.—Add 10 c.c. of concentrated sulphuric acid to 200 c.c. of water, and allow the mixture to stand till it becomes quite cold; now add little by little, with constant stirring, about 30 grammes of barium peroxide. Allow to settle, and decant off the clear liquid. It is a dilute solution of hydrogen peroxide, and the following experiments may be performed with it—

(1) To some of the liquid add potassium iodide, iodine will be liberated, and the solution become brown. The equation for the reaction which takes place has been given in § 122.

(2) Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt, say the acetate, and then exposing this to sulphuretted hydrogen. Steep the paper in a little of the hydrogen peroxide solution and it will become white, the black sulphide of lead having been transformed into the white sulphate, as shown in the equation given above.

(3) Add silver nitrate to some of the solution, and then caustic soda; a black precipitate of hydrated oxide of silver will be formed, and this in contact with the hydrogen peroxide will undergo decomposition in the manner already described; the effervescence of gas which is seen to occur may be shown to be due to oxygen.

125. **Proof of the Composition of Hydrogen Peroxide.**—The following method may be adopted to prove that the ratio of oxygen to hydrogen in hydrogen peroxide is twice as great as it is in water:—A given weight (about 0·2 gramme) of the pure substance, prepared as already described, is introduced into a flask, which is then filled up completely with recently-boiled water. This flask is provided with a delivery tube which does not reach below the bottom of the cork, and is also filled with water. The flask is heated at first to about 80° C., but finally (when the evolution of gas slackens) to the boiling-point. Oxygen is evolved, and is collected over water in a measuring tube of about 100 c.c. capacity. The weight of oxygen evolved can be calculated from its volume, and if the hydrogen peroxide is pure it will be found that 34 parts by weight of it yield 16 parts by weight of oxygen. The remaining $34 - 16 = 18$ parts by weight consist of water. Now 18 parts by weight of water contain 16 parts by weight of oxygen and 2 parts by weight of hydrogen. Therefore the ratio of oxygen to hydrogen in hydrogen peroxide is $2 \times 16 : 2 = 16 : 1$, which is twice as great as the ratio in water (approximately $8 : 1$).

The simplest formula for hydrogen peroxide would be HO, for 1 and 16 are the atomic weights of hydrogen and oxygen. It has been proved, however, by a physical method of determining molecular weights (the lowering of freezing-point method), that the molecular weight is not 17 as it would be if the formula were HO, but 34, which corresponds to the formula H_2O_2. The doubled formula possesses the advantage that it fits in with the usual valencies of hydrogen (one) and oxygen (two). Thus the structural formula would be—

$$H-O-O-H.$$

If however the single formula were adopted, both oxygen and hydrogen must have the same valency, the structural formula being $H-O$.

QUESTIONS.—CHAPTER XIII.

1. Describe carefully a synthetic method of determining the composition of water by volume.
2. How may the volumetric composition of water be determined analytically?
3. In a determination of the volumetric composition of water by Bunsen's method the following readings were taken—

   Distance of closed end of tube from mercury in trough (Neglect any slight changes.) 72 c.m.
   Height of column of mercury above mercury in trough after introduction of oxygen . 54 c.m.
   Height of column of mercury above mercury in trough after introduction of hydrogen . 14 c.m.
   Height of column of mercury above mercury in trough after explosion and cooling to atmospheric temperature . . . 23·85 c.m.
   Temperature of the air throughout the experiment . . . . . 16° C.
   Atmospheric pressure throughout the experiment . . . . . 75 c.m.
   Pressure of aqueous vapour at 16° C. . 1·35 c.m.

   Calculate the volume of hydrogen combined with 1 volume of oxygen.
4. How would you prove by experiment that steam contains its own volume of hydrogen?
5. Describe the method by which Dumas and Stas determined the composition of water by weight.
6. Pure hydrogen is passed over heated oxide of copper, and the water which forms is collected; if the loss in weight of the oxide of copper be 4·20 grammes, and

the weight of the water obtained 4·73 grammes, determine the amount of hydrogen and oxygen in 100 grammes of water.

7. Trace the changes in volume that occur when heat is applied to a mass of ice until it melts and passes into vapour.
8. Define the *unit quantity of heat.* What name is given to this unit?
9. What is meant by "specific heat"? The specific heat of air is 0·24; find how much the temperature of a cubic metre of air will be raised by the heat given off during the cooling of 100 grammes of water from 25° C. to 20° C.
10. A kilogramme of water at 0° C. is intimately mixed with a kilogramme of mercury at 100° C., until both acquire the same temperature; the specific heat of mercury being 0·033, find the increase in temperature of the water.
11. What do you understand by the term "latent heat"? Under what circumstances does heat become latent, and what becomes of the heat thus rendered latent?
12. How much ice at 0° C. will a kilogramme of mercury at 100° C. just suffice to melt?
13. How many units of heat are required to raise the temperature

    (*a*) of 100 grammes of water 10 C°.;
    (*b*) " " " " mercury 10 C°.;

    and to convert 100 grammes of water at 0° C. into steam at 100 C°.?
14. Describe an experiment showing that water vapour exerts a pressure at ordinary temperature.
15. Explain what is meant by the *boiling-point of a liquid.*
16. When is a solution said to be *saturated?* What amount of potassium nitrate (see table, § 115) would be required to form a saturated solution in 150 c.c. of water, (*a*) at zero, (*b*) at 50° C.?

17. State Henry's Law. What volume of CO_2 will dissolve in 250 c.c. of water under standard pressure, (*a*) at zero, (*b*) at 20° C., and what at these temperatures when the pressure is that of 76 mm. of mercury, and when it is three atmospheres?
18. A mixture of carbon dioxide and oxygen containing 95 per cent. by volume of the latter gas is shaken up with 500 c.c. of water at standard temperature and pressure; what volume of each gas will be dissolved?
19. In what respects does a typical sample of rain-water differ from the water of the Thames?
20. How does it come about that sea water contains more matter in solution than river water?
21. What are the essential qualities of good drinking water?
22. Why is more soap required to produce a permanent lather with *hard* water than with *soft* water?
23. State the constituents to which the temporary and permanent hardness of water are respectively due.
24. Explain the circumstances under which the addition of lime-water renders a water soft, and state why it does so.
25. How can calcium carbonate be made to dissolve freely in water, and how may the calcium carbonate be precipitated out of such water again without the addition of chemical reagents?
26. How can permanent hardness be removed from water?
27. How can the temporary and permanent hardness in a sample of water be determined?
28. What is meant by *water of crystallisation?* Give examples.
29. Distinguish between a *hydrate* and a *hydroxide*, and give examples of each.
30. Write down in separate paragraphs (*a*) the physical, (*b*) the chemical properties of water.
31. Make a list of those properties of water which you regard as being absolutely characteristic of that body.
32. How would you test whether a given colourless liquid is water or not?

33. Describe how you would test the purity of a sample of water.

34. How is hydrogen peroxide prepared? What is its action on (1) potassium iodide, (2) lead sulphide, (3) silver oxide?

35. It has been said that hydrogen peroxide behaves both as an oxidising and a reducing agent; explain this statement, and illustrate your remarks by references to reactions.

36. How can the composition of hydrogen peroxide be proved?

CHAPTER XIV.

THE HALOGENS.

126. A COMPARISON of the physical and chemical properties of the four elements, fluorine, chlorine, bromine and iodine, and of their compounds, readily leads one to regard these elements as forming a natural group.

This is shown in two ways, firstly by the *resemblance* in properties, and secondly by the *gradual transition* in their properties, which proceeds always in the same order, viz. in the order of their atomic weights. A general survey of the group will illustrate this.

Physical Properties of these Elements.—Fluorine is a gas which condenses to a liquid when cooled to a temperature of − 187° C.; it possesses a very faint greenish-yellow colour; chlorine is a much more readily-condensible gas, and has a distinct greenish colour; bromine is a dark red liquid boiling at 59° C. and solidifying at − 7° C.; whilst iodine is a black crystalline solid which boils at 184° C., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane, which is, however, much less marked in the case of iodine than in that of the other three elements. The halogens have an odour resembling that of seaweed if they are in a largely-diluted condition.

Their solubility in water follows the order of their atomic weight as far as chlorine and iodine are concerned, but bromine is an exception, whilst fluorine decomposes water. Thus chlorine dissolves in about half its volume of water, whilst iodine is only very slightly soluble. Bromine, however, dissolves to the extent of 3 parts in 100 by weight, which corresponds to about 4 volumes of bromine as vapour in 1 volume of water.

When chlorine is passed into water to saturation at 0° C., yellow crystals having the composition $Cl_2 \cdot 8\ H_2O(?)$ separate out. On warming these crystals they readily decompose with the evolution of chlorine. Bromine under similar circumstances forms crystals having the composition $Br_2 \cdot 10\ H_2O(?)$.

127. **General Chemical Properties.**—All the halogens combine directly with hydrogen to form gases (except hydrofluoric acid, which is a liquid boiling at 19·5° C.). These hydrides of the halogens are very soluble in water, giving rise to strongly acid solutions. The readiness with which combination with hydrogen takes place *decreases* as the atomic weight *increases*. Thus, fluorine and hydrogen combine even in the dark and at very low temperatures, whereas chlorine requires the influence of heat or of chemically active light rays, and bromine and iodine are induced to combine with hydrogen with much greater difficulty.

Moreover, the stability of the products, HF, HCl, HBr, HI, shows a falling off in the order named.

The hydrogen atom of each of these compounds can be replaced by the metals potassium and sodium to form a group of bodies, KF, NaF, KCl, etc., all of which closely resemble *sea-salt*. It is from this that the name *halogens* is derived (ἅλς, sea-salt, and γεννάω, I produce).

The tendency of the halogens to combine with oxygen *increases* as the atomic weight *increases*. Thus, whilst fluorine forms no oxide, and chlorine can only be made to combine with oxygen indirectly giving rise to unstable oxides, iodine is directly oxidised by nitric acid, and its oxide is much more stable. Bromine occupies an anomalous position here, as no oxide of it is known.

The interaction of the halogens and water affords another example of this gradation in properties as we pass from fluorine to iodine. Fluorine decomposes water immediately at ordinary temperatures, a vigorous reaction taking place; much of the oxygen liberated is in the form of ozone. Chlorine and bromine act on water at ordinary temperatures only in the presence of sunlight, and no ozone is formed; chlorine is much the more active of the two. Iodine does not decompose water.

CHLORINE, Cl_2.

128. **Occurrence.**—Chlorine occurs very abundantly in nature, but never in the free state. Its most important compound is common salt (sodium chloride), which forms large deposits in various parts of the world, *e.g.* Cheshire in England, and Wieliczka in Galicia. Common salt is also the chief solid constituent of sea water. The enormous salt deposits at Stassfurt in Germany are composed largely of the chlorides of potassium and magnesium. Free hydrochloric acid is a constituent of the gastric juice.

129. **Preparation.**—Chlorine is usually prepared in the laboratory by heating manganese dioxide with concentrated hydrochloric acid. The reaction which takes place is represented by the equation—

$$\underset{\text{Manganese dioxide.}}{MnO_2} + 4\,HCl = \underset{\text{Manganous chloride.}}{MnCl_2} + 2\,H_2O + Cl_2.$$

Exp. 100.—Introduce about 100 grammes of manganese dioxide, in small lumps, into a large flask, and just cover it with strong hydrochloric acid. Close the mouth of the flask with an india-rubber cork carrying a safety funnel and delivery tube. Support the flask on a sand-bath by means of a retort-stand, and connect it with a wash-bottle containing a little water. Provide the wash-bottle with a delivery tube reaching to the bottom of a glass cylinder as shown in Fig. 36. Now apply a gentle heat to the flask, when chlorine is evolved mixed with hydrochloric acid. For a short time, both the chlorine and the hydrochloric are absorbed by the water in the wash-bottle. Soon, however, the solution becomes saturated with chlorine which then passes on, whilst the hydrochloric acid, being very much more soluble, continues to be absorbed in the wash-bottle. The chlorine is collected in glass cylinders by displacement of air; it cannot be collected over water or mercury because it is soluble in the former and attacks the latter; it may, however, be collected over strong brine in which it is only slightly soluble.

If the gas is required *dry* it may be passed through one or more wash-bottles containing concentrated sulphuric acid before being collected as above.

Instead of using hydrochloric acid in the preparation of chlorine just described, a mixture of common salt and strong sulphuric acid may be employed. The equation representing the reaction which takes place then becomes—

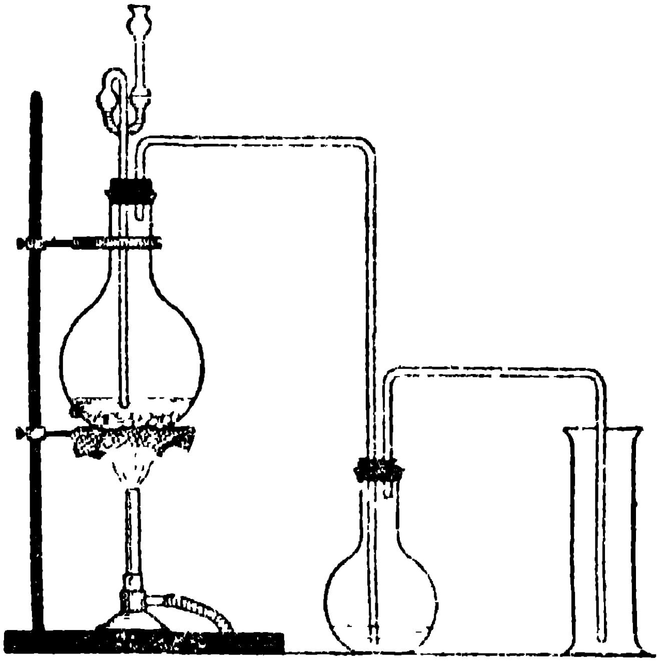


FIG. 36.

$$MnO_2 + 3\ H_2SO_4 + 2\ NaCl = MnSO_4 + 2\ NaHSO_4 + 2\ H_2O + Cl_2.$$

The most convenient method of preparing chlorine is to act on bleaching powder with dilute hydrochloric acid. The bleaching powder is used in the form of small lumps, obtained by first pressing it into a cake and then breaking this cake up. Under these conditions chlorine is evolved at a convenient rate without the application of heat—

$$\underset{\text{Bleaching powder.}}{CaOCl_2} + 2\ HCl = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + Cl_2.$$

130. Properties.—Chlorine is a greenish-yellow gas which has a very irritating action on the mucous membrane. It is soluble in water, one volume of which takes up about two volumes of the gas at ordinary temperatures. Chlorine is a heavy gas, its density being about two and a half times that of air. Its molecule contains two atoms, except at very high temperatures, when partial dissociation into single atoms takes place, as shown by the fall in vapour density.

Chlorine is a very active substance. It combines directly with many elements and compounds at the ordinary temperature, very frequently with incandescence.

131. Combination of Chlorine and Hydrogen.—When chlorine and hydrogen are mixed and exposed to direct sunlight they combine with explosion, hydrochloric acid being formed. Burning magnesium wire, which gives out light very rich in chemically active rays, also causes the mixture to explode. In diffused daylight combination takes place gradually, and in the dark hydrogen and chlorine do not unite. By proceeding as described in the following experiment it is possible to burn hydrogen quietly in chlorine.

Exp. 101.—Prepare a jar of chlorine from manganese dioxide and hydrochloric acid as described above, and introduce a lighted jet of hydrogen into it. It continues to burn with the production of fumes of hydrochloric acid, which may be made more visible by bringing a drop of ammonia liquor to the mouth of the jar.

The affinity of chlorine for hydrogen is so great that it is able to extract it from many compounds, such as turpentine ($C_{10}H_{16}$), sulphuretted hydrogen (H_2S) and water.

Exp. 102.—Introduce a piece of blotting-paper soaked in turpentine into a jar of chlorine. The turpentine takes fire; white fumes of hydrochloric acid are formed and a black deposit of free carbon settles on the sides of the jar.

$$C_{10}H_{16} + 8\ Cl_2 = 10\ C + 16\ HCl.$$

Exp. 103.—Pass chlorine for some minutes through about 50 c.c. of water, and to about 20 c.c. of this add a solution of sulphuretted hydrogen; hydrochloric acid is formed, the liquid becoming turbid owing to the separation of sulphur, according to the equation—

$$Cl_2 + H_2S = 2\ HCl + S.$$

Exp. 104.—Fill a Cowper's tube with chlorine water (see Fig. 37) and expose to direct sunlight; bubbles of gas will be seen to rise in the liquid. When sufficient gas has collected it may be tested with a glowing splinter, and will be found to be oxygen. The change which has taken place is represented by the equation—

$$8\,Cl_2 + 8\,H_2O = 14\,HCl + 2\,HClO_3 + O_2.$$

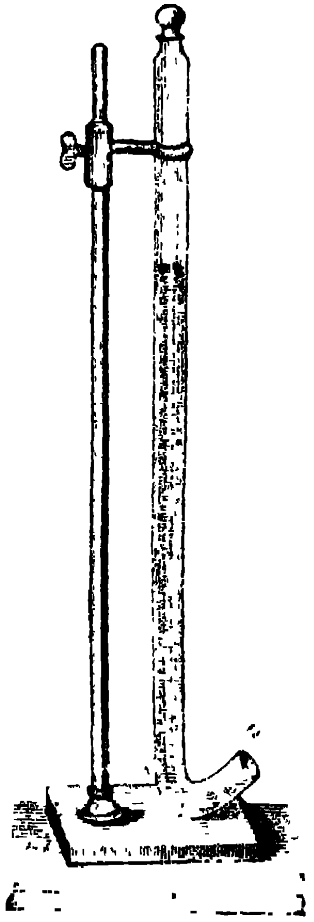


FIG. 37.

Chlorine will, moreover, support the combustion of a candle or of coal gas, on account of its affinity for hydrogen. The substances of which candles are composed consist either entirely, or at any rate largely, of carbon and hydrogen, and when a lighted candle is lowered into a jar of chlorine it continues to burn with formation of hydrochloric acid and separation of carbon, just as in the case of turpentine.

Exp. 105.—Fix a piece of candle into a deflagrating spoon, light it, and lower into a jar of chlorine. The candle continues to burn with a dull red smoky flame and soot is deposited on the walls of the jar.

Coal gas, again, consists almost entirely of a mixture of free hydrogen and compounds of carbon and hydrogen, and when a jet of lighted coal gas is lowered into a jar of chlorine it continues to burn, but the flame becomes duller and smoky owing to the separation of free carbon.

132. Combination of other Elements with Chlorine.—

Exp. 106.—Into a jar of chlorine bring a piece of phosphorus on a deflagrating spoon and without the application of heat; presently the phosphorus will ignite and burn feebly with the formation of phosphorus trichloride—

$$P_4 + 6\,Cl_2 = 4\,PCl_3.$$

Antimony, copper and some other metals in a finely-divided condition also ignite when plunged into chlorine.

Exp. 107.—Heat a piece of sodium in a deflagrating spoon until it takes fire, and then plunge it into a jar of chlorine; the sodium burns brilliantly, uniting with the chlorine to form sodium chloride.

Inactivity of Dry Chlorine.—It is found that, though, as we have seen, moist chlorine is a very active substance, *perfectly dry* chlorine is comparatively inactive. Thus, sodium even when heated does not combine with dry chlorine. Here, then, we meet with another example of the phenomenon already encountered in the case of hydrogen and oxygen, that the presence of water is necessary in order that a chemical reaction may take place.

133. **Oxidising Action of Chlorine.**—Chlorine is a strong oxidising agent *in the presence of moisture*, this property depending on its power of combining with the hydrogen of water and liberating *nascent* oxygen. An example of such action is its power of converting sulphurous acid into sulphuric acid.

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + H_2O + Cl_2 = \underset{\text{Sulphuric acid.}}{H_2SO_4} + 2\ HCl.$$

Another example is furnished by the *bleaching* properties of chlorine; vegetable colouring matters, *e. g.* the pigments in the leaves and flowers of plants are deprived of their colour by moist chlorine, though in the absence of moisture no such action takes place.

Exp. 108.—Prepare a jar of dry chlorine (using two sulphuric acid wash-bottles). Place in this a piece of cloth dyed with turkey-red and leave it some minutes with the cover on; no decolorisation will occur, but on moistening the cloth it will be bleached.

134. **Action of Chlorine on Organic Substances.**—Many organic substances are very readily attacked by chlorine. In some cases (*e. g.* ethylene) the chlorine simply adds itself on to the compound, and *addition products* are formed. In other cases (*e. g.* marsh gas) chlorine replaces one or more atoms of hydrogen, and *substitution products* result: the

displaced hydrogen combines with more chlorine forming hydrochloric acid. We shall return to this subject when studying the hydrocarbons (see Chap. XXII.).

Chlorine is a very powerful *disinfectant*, as it rapidly kills the minute forms of life known as bacteria, which are the chief cause of the putrefaction of organic matter.

135. **Chlorine Hydrate.**—This substance is produced by passing chlorine into a mixture of water and ice. It is a greenish crystalline compound of uncertain composition, best represented by the formula $Cl_2 \cdot xH_2O$, where x is either 8, 9 or 10. At ordinary temperature it decomposes into chlorine and water.

136. **Liquid Chlorine.**—Chlorine can readily be liquefied as described in § 29. Liquid chlorine is an orange-yellow substance of specific gravity 1·66; it boils at $-33·6°$ C. It is prepared commercially for use in extracting gold.

BROMINE, Br_2.

137. **Occurrence.**—Bromine does not occur in the free state in nature. It is found in small quantities in combination with certain metals, chiefly potassium, sodium, magnesium and calcium, in sea water and in many mineral waters. The salt deposits of Stassfurt contain a small percentage of bromides, and it is from this source that most of the bromine of commerce is obtained.

138. **Preparation.**—Bromine may be prepared from sodium bromide or potassium bromide by heating with strong sulphuric acid and manganese dioxide, just as chlorine is prepared from common salt.

$$2\ KBr + 3\ H_2SO_4 + MnO_2 = 2\ KHSO_4 + MnSO_4 + 2\ H_2O + Br_2.$$

Exp. 109.—Introduce into a tubulated retort a mixture of about 20 grammes of potassium bromide and 10 grammes of manganese dioxide. Cover the mixture with strong sulphuric acid poured in through a funnel inserted in the tubulus of the retort. Insert the stopper and place over the open end of the retort a flask resting in a trough of water and covered over with a wet cloth, as shown in the diagram (Fig. 38). On gently heating the mixture bromine distils over and condenses in the cooled receiver, where it collects as a dark-red liquid. Since the vapours of bromine are very injurious, the operation *must* be performed in a fume cupboard with a *good draught*.

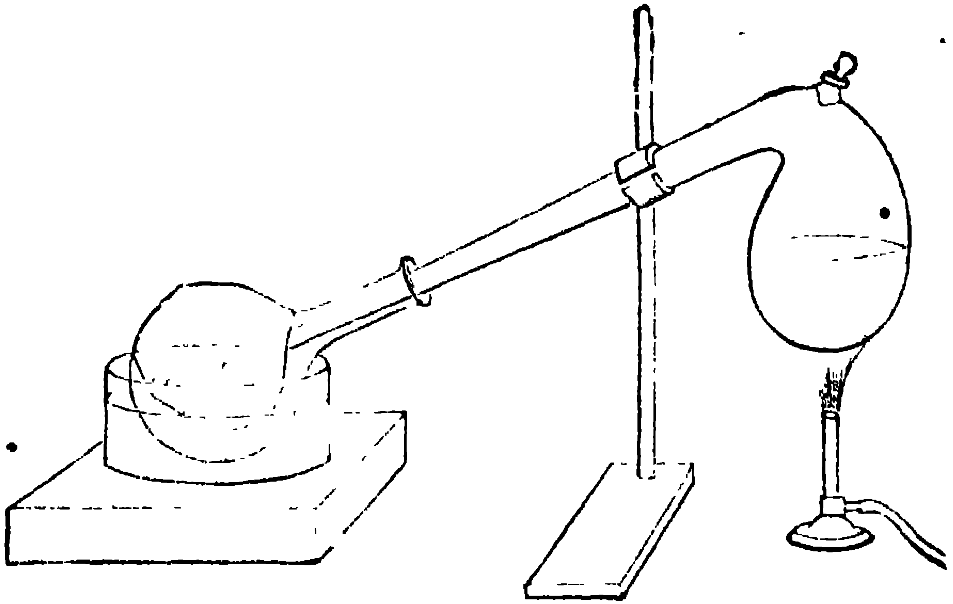


FIG. 38.

* 139. **Properties.**—Bromine is a heavy, mobile, dark-red liquid, possessing a very offensive odour (hence its name from βρῶμος = a stench). Its action on the mucous membrance is worse even than that of chlorine. Bromine has a specific gravity of 3·188 (water = 1) at 0° C., and it boils at 59° C., the vapour possessing the same colour as the liquid. At ordinary temperatures bromine rapidly evaporates if exposed in an open vessel.

Bromine is soluble in a number of liquids giving reddish-brown solutions; the chief are—water, alcohol, ether, acetic acid, carbon disulphide, and chloroform. At 0° C. 1 gramme of water dissolves 0·036 gramme of bromine; the solubility in the other liquids mentioned is considerably greater.

Exp. 110.—Test the solubility of bromine in some or all of the above liquids (using the bromine you prepared in the last experiment). By adding the bromine drop by drop to equal volumes of each of the liquids (say 5 c.c.), shaking up after each addition, and noting when further solution ceases (as shown by the bromine remaining undissolved at the bottom of the liquid), a rough comparison of its solubility in the different solvents can be made.

Bromine, like chlorine, contains two atoms in its gaseous molecule, except at high temperature, when partial dissociation into free atoms takes place. The dissociation is, however, much more complete with bromine than with chlorine.

As regards its chemical properties, bromine behaves like chlorine, but is generally much less active. Thus, many metals and non-metals combine readily with bromine, some (*e. g.* arsenic) with evolution of so much heat that they take fire. The action of bromine on phosphorus is, indeed, so violent that it is advisable to moderate it by dissolving the bromine in three times its volume of carbon bisulphide.

Bromine and hydrogen do not combine directly at ordinary temperature, but combination can be brought about by the application of heat, *e. g.* by passing the mixed gases through a red-hot tube. A solution of bromine in water (called *bromine water*) gradually decomposes in sunlight with evolution of oxygen and formation of hydrobromic acid—

$$2\,Br_2 + 2\,H_2O = 4\,HBr + O_2.$$

The decomposition is, however, much slower than with chlorine.

As we should expect from what has just been said, bromine water acts as a mild oxidising agent and exhibits feeble bleaching properties, its action being explained exactly as in the case of chlorine. It is much used as an oxidising agent in analytical chemistry. Bromine readily attacks organic substances such as starch and the skin, turning them *yellow.*

Exp. 111.—Add a drop of bromine water to some starch and note the yellow colour developed.

Bromine is readily displaced from its compounds with metals by the more active element chlorine. The following experiment should be performed to illustrate this.

Exp. 112.—Add some chlorine water to a solution of potassium bromide : not he red col our developed. Shake up the liquid with a little carbon disulphide. The bromine dissolves in it and the red solution collects at the bottom of the vessel.

$$2\,KBr + Cl_2 = 2\,KCl + Br_2.$$

Bromine is used in photography and in medicine, and also as a disinfectant.

Bromine Hydrate.—Bromine combines with water at low temperatures, forming a compound, $Br_2 \cdot xH_2O$, corresponding to chlorine hydrate.

IODINE, I_2.

* 140. **Occurrence.**—Iodine is not found free in nature, but its compounds with the metals potassium, sodium, magnesium and calcium are widely distributed, though they do not occur in large quantity at any one place. Thus sea water and the plants and animals which inhabit the sea, notably sea-weed, contain small quantities of iodides, as also do many mineral waters. The crude sodium nitrate (caliche), found in such abundance in Chili and Peru, contains small quantities of sodium iodate, and this is now the chief source of the element.

* 141. **Preparation.**—In the laboratory iodine is prepared in a similar manner to bromine, namely, by heating potassium or sodium iodide with manganese dioxide and strong sulphuric acid—

$$2\,KI + 3\,H_2SO_4 + MnO_2 = 2\,KHSO_4 + MnSO_4 + 2\,H_2O + I_2.$$

This method is, as we have seen, a general one for the preparation of the halogens, except fluorine, and the reaction may be represented thus—

$$2\,XR + 3\,H_2SO_4 + MnO_2 = 2\,XHSO_4 + MnSO_4 \\ + 2\,H_2O + R_2$$

where X = K or Na and R = Cl, Br or I.

Exp. 113.—Prepare iodine by following the directions in Exp. 109, using potassium iodide in place of potassium bromide. The same apparatus should be used, but it will not be necessary to cool the receiver by cold water. Some of the iodine will probably condense in the neck of the retort; it can be driven into the receiver by gently warming with a Bunsen burner.

*** 142. Properties.**—Iodine is a lustrous crystalline black solid of specific gravity 4·95. It melts at 113° C., and boils at 184° C., forming a deep violet vapour; at ordinary temperatures, however, iodine slowly undergoes vaporisation. The density of iodine vapour is very high, being about eight and a half times as great as that of air, and 126 times that of hydrogen. This corresponds to a molecular weight of 2 × 126 = 252, which is about twice the atomic weight of iodine, so that the gaseous molecule of iodine contains two atoms. This is only true up to 450° C., however, for above this temperature the density gradually falls, till at 1,500° C. its value is reduced by nearly one-half, showing that most of the molecules have been broken down into single atoms—

$$I_2 = I + I.$$

We have seen that chlorine and bromine behave in a similar manner, but the decomposition is much less complete than in the case of iodine. Since bromine is decomposed to a greater extent than chlorine, we have here another property which follows the order of the atomic weights of the three elements.

Iodine is only slightly soluble in water, 100 grammes of which dissolve 0·02 gramme of the element, but many other liquids dissolve it in much greater quantity. These solvents may be divided into two classes, according as the colour of the solution they produce is reddish-brown or violet; to the former class belong water, potassium iodide, alcohol, and ether; and to the latter, carbon disulphide, chloroform, and liquid hydrocarbons.

Exp. 114.—Introduce a crystal of iodine into about 5 c.c. of each of the liquids mentioned above (as an example of a liquid hydrocarbon you can use benzene). You will notice that in all these liquids, except water, a deeply-coloured solution is rapidly formed; the water is only coloured slightly brown.

Observe that the colours of the different solutions correspond with those stated above.

*** 143. Action of Iodine on other Elements.**—Iodine is not nearly such an active substance as the other halogens, but it nevertheless combines directly with many elements, both metals and non-metals, often, indeed, without the application of heat. For example, mercury and iodine will unite on merely rubbing them together; again, on bringing together phosphorus and iodine, the phosphorus first melts and then combination takes place with so much energy that the mixture bursts into flame. When antimony powder is thrown into iodine vapour it takes fire; and on heating potassium and iodine together they unite with explosive violence.

Hydrogen and iodine combine directly with even greater difficulty than hydrogen and bromine, the temperature necessary being much higher; the combination is facilitated by the presence of spongy platinum, which acts as a catalytic agent. As we should expect from this, iodine in the presence of water has no bleaching properties.

* 144. **Displacement of Iodine from its Salts.**—Just as chlorine displaces bromine from its compounds, illustrating thereby its greater activity, so both chlorine and bromine will displace iodine from its compounds. For example, on treating potassium iodide with either chlorine or bromine, free iodine is liberated—

$$2\ KI + Cl_2 = 2\ KCl + I_2.$$
$$2\ KI + Br_2 = 2\ KBr + I_2.$$

Exp. 115.—Add a few drops of chlorine water to about 10 c.c. of a solution of potassium iodide. The solution will turn reddish-brown, owing to the liberated iodine dissolving in the excess of potassium iodide. Now shake up with a little carbon bisulphide. This will dissolve out the iodine, forming a violet solution which will collect at the bottom of the vessel.

A similar experiment may be performed using bromine water in place of chlorine water.

* 145. **The "starch test" for Iodine.**—Iodine forms a very characteristic blue compound with starch. On heating, the compound is decomposed and the colour disappears, but on cooling recombination takes place and the colour reappears.

Exp. 116.—Shake a very little starch in a test-tube of cold water and boil well; add a few drops of a solution of iodine in potassium iodide; a blue colour is formed. Boil the blue solution, and the blue colour disappears, reappearing on cooling.

* 146. **Uses.**—Iodine is largely employed in medicine for taking down glandular swellings. It was at one time thought that the iodine must be applied in the free state, and an alcoholic solution was (and still is) used; it has recently been found, however, that potassium iodide is quite as effective, and as it does not leave any stain on the skin its employment is preferable.

Iodine in the form of potassium iodide is also used as a tonic. Further, a compound of iodine with carbon and hydrogen, called iodoform (CHI_3), finds wide application as an antiseptic.

QUESTIONS.—CHAPTER XIV.

1. Draw up in tabular form a comparison between the halogen elements with regard to—(*a*) their colour, (*b*) their solubility in water, (*c*) their action on water, (*d*) their affinity for hydrogen.
2. Describe how you would prepare and collect a jar of dry chlorine. Sketch the apparatus you would employ.
3. Describe experiments illustrating the great affinity of chlorine for hydrogen.
4. Describe the chemical changes which accompany the burning of a candle in chlorine, and show how far they account for the peculiar appearance of the flame which is observed when a candle burns in chlorine.
5. Describe experiments illustrating the *oxidising action* of chlorine.
6. Under what conditions does chlorine act as a bleaching agent?

* 7. Describe exactly how you would prepare bromine from potassium bromide, and give a sketch of the apparatus you would employ.

* 8. Name some liquids which dissolve bromine and iodine, and state the colour of the solution produced in each case. Compare the action of these two halogens on starch.

9. What is the action of chlorine on solutions of sodium bromide, potassium iodide and sulphuretted hydrogen respectively?

*10. Describe the action, if any, which takes place when sulphur, phosphorus, carbon, silicon and sulphuretted hydrogen are respectively brought into contact with iodine.

11. By what general method can the halogens (except fluorine) be prepared?

CHAPTER XV.

COMPOUNDS OF HYDROGEN WITH THE HALOGENS.

147. HYDROGEN forms one compound with each of the halogens. These compounds are all gases at the ordinary temperature, except hydrogen fluoride, which is a very volatile liquid. They are all very soluble in water, producing strongly acid solutions. It will be convenient, for purposes of terminology, to use the terms *hydrogen fluoride*, *hydrogen chloride*, etc., for the gaseous acids (or anhydrous liquids), reserving the expressions *hydrofluoric acid*, *hydrochloric acid*, etc., for the aqueous solutions of the hydrides.

HYDROGEN CHLORIDE OR HYDROCHLORIC ACID, HCl.

148. **Occurrence.**—Hydrogen chloride is one of the gaseous products of the eruption of volcanoes.

Preparation.—Hydrogen chloride is most conveniently prepared by the action of concentrated sulphuric acid on common salt (sodium chloride).* The gas is evolved in the cold with effervescence, but much more rapidly on gently heating; the following reaction takes place—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Hydrogen chloride cannot be collected over water, in which it is very soluble; it may however be collected by downward displacement of air or over mercury.

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* All chlorides except silver chloride and mercurous chloride yield hydrochloric acid when heated with sulphuric acid.

Exp. 117.—The apparatus required for the preparation of hydrogen chloride is sketched in Fig. 39. Introduce into the flask some common salt, and fill the wash-bottle about one-third full of concentrated sulphuric acid. Connect up the apparatus as shown and pour concentrated sulphuric acid slowly down the thistle funnel till it just covers the salt. Warm *gently* and collect the gas, which is dried by the sulphuric acid in the wash-bottle, in glass cylinders or other vessels as required. If the gas is wanted *pure* and *quite dry* it should be passed through two sulphuric acid wash-bottles and collected over mercury.

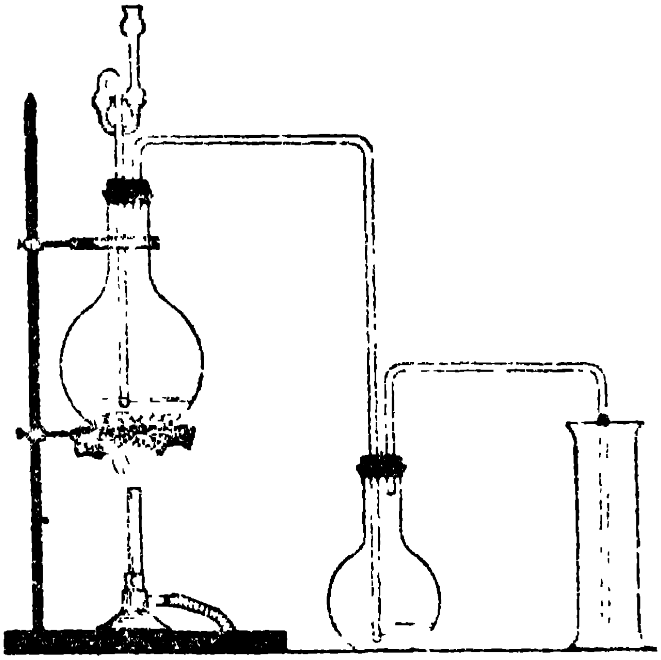

FIG. 39.

149. **Properties.**—Hydrogen chloride is a colourless gas which fumes in moist air and has a strongly irritant action on the mucous membrane. Its density is 18·2 (H = 1), and it is therefore about $1\frac{1}{4}$ times as heavy as air.

Hydrogen chloride is extremely soluble in water, 1 c.c. of which at 0° C. dissolves 503 c.c. of the gas, and at ordinary temperatures about 450 c.c. The solution of the gas is accompanied by a considerable evolution of heat, and there is also an increase in the volume of the liquid. The following experiment illustrates in a striking manner the great solubility of hydrogen chloride.

Exp. 118.—Fill a large dry flask, of at least two or three litres content, with hydrogen chloride gas by displacement. Fit it with an india-rubber cork, through which passes a tube with stopcock, and drawn out into a jet as shown in Fig. 40. Dip the extreme end of the tube into water and open the stopcock.

Under these conditions the gas at first only comes into contact with the water very slowly by a process of diffusion, and it is desirable to bring about contact with a larger surface of water by cooling the flask; this may be done by pouring a few drops of ether over its surface. When the water reaches the top of the tube and overflows into the flask, the first few c.c. of water dissolve the whole of the gas, and the rest of the water rushes up through the tube with great force to fill the vacuum in the flask.

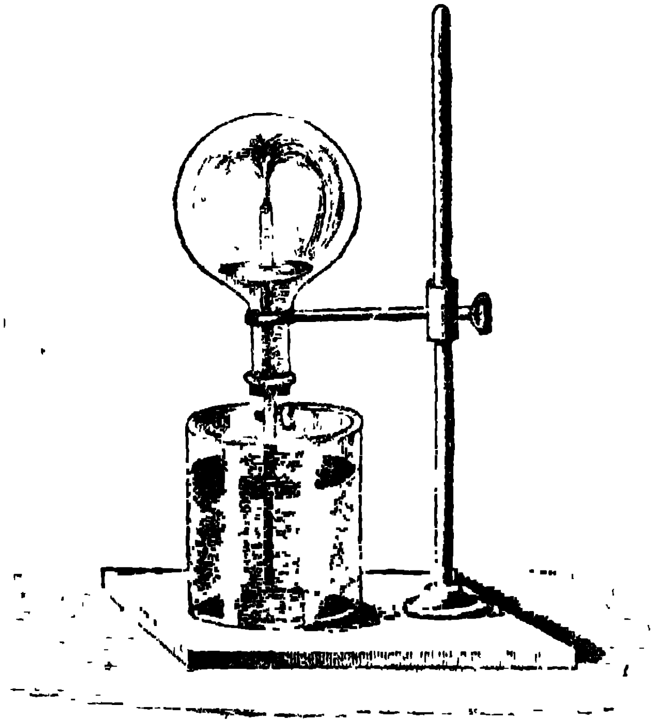

Fig. 40.

Hydrogen chloride is not combustible nor is it a supporter of combustion.

Exp. 119.—Introduce a lighted taper into a jar of the gas. The flame is extinguished and the gas does not burn. Try similar experiments with burning sulphur and phosphorus; these are also extinguished.

The gas attacks many metals, especially when heated, with liberation of hydrogen and formation of a chloride of the metal.

Exp. 120.—Place some zinc in a short piece of combustion tubing; heat it, and pass hydrogen chloride over it. Collect the gas given off over water. Test it with a lighted taper; it is hydrogen. The white residue left in the tube is zinc chloride, $ZnCl_2$.

$$Zn + 2\ HCl = ZnCl_2 + H_2.$$

Similar experiments may be performed with other metals, *e.g.* iron and magnesium.

Hydrogen chloride also reacts with many metallic oxides, especially when heated. If the oxide is a *basic oxide*, water and a chloride of the metal are the products; an experiment (Exp. 86) illustrating this has already been performed; *peroxides*, on the other hand, give rise to free chlorine, together with water and a chloride of the metal.

Exp. 121.—Proceed exactly as described in Exp. 86, using manganese dioxide instead of lime. Test the issuing gas, which is yellowish-green in colour, with moist litmus paper; it is bleached. The gas is chlorine.

The equation representing the change which takes place is the same as that we have already met with in the preparation of chlorine, viz.—

$$MnO_2 + 4\ HCl = MnCl_2 + 2\ H_2O + Cl_2.$$

When the gas is brought into contact with ammonia gas direct combination takes place with formation of dense white fumes of ammonium chloride (NH_4Cl) unless the gases are *quite dry*—

$$NH_3 + HCl = NH_4Cl.$$

150. **Analytical proof of the Composition of Hydrogen Chloride.**—We can prove that hydrogen chloride contains half its volume of hydrogen by acting on it with metallic sodium, when the chlorine is extracted and combines with the sodium forming sodium chloride—

$$2\ HCl + 2\ Na = 2\ NaCl + H_2.$$

The sodium is most conveniently used in the form of a solution in mercury (called *sodium amalgam*), and the experiment may be carried out as follows:—

Exp. 122.—About 50 c.c. of hydrogen chloride are introduced into the closed limb of a bent eudiometer tube previously filled with mercury (Fig. 41). The levels of mercury in the two limbs are made equal by running mercury out of the tap or pouring more into the open limb, and the volume of gas is measured. Mercury is now allowed to run out of the tap till very little is left in the open limb and the latter is filled up with liquid sodium amalgam. The open end is then closed by the thumb and the hydrogen chloride transferred to the other limb by inverting and suitably manipulating the apparatus. The eudiometer is now restored to its normal position and then again inverted so as to bring the gas intimately in contact with the amalgam. Finally the gas is restored to the closed limb, and liquid is run out through the tap till the levels in the two limbs are equal. The volume of gas which remains will be found to be half that originally taken, and it may be proved to be hydrogen by the usual tests.

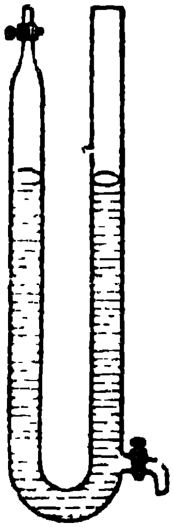

FIG. 41.

To prove that the volumes of chlorine and hydrogen which combine to form hydrogen chloride are equal, an aqueous solution of the gas may be submitted to electrolysis.

Exp. 123.—The experiment is carried out in the apparatus shown in Fig. 42, which consists of a three-limbed glass vessel, the two side limbs being provided with stopcocks and the central one with a funnel. At the base of the side limb are the electrodes which are connected to the poles of a battery. The negative electrode, at which hydrogen is evolved, may be made of platinum, but since chlorine acts on platinum the positive electrode must be made of gas carbon. Strong hydrochloric acid is introduced through the funnel till the side tubes are full, and an electric current is passed through the liquid with the stopcocks open till the liquid in the limb containing the positive electrode is saturated with chlorine; the hydrogen liberated in the other limb being almost insoluble escapes meanwhile through the open stopcock. The stopcocks are now closed, and the gases will be found to collect in equal volumes in the two limbs. Their identity may be proved by the usual tests.

From the results of these two experiments it follows that two volumes of hydrogen chloride consists of one volume of hydrogen and one volume of chlorine.

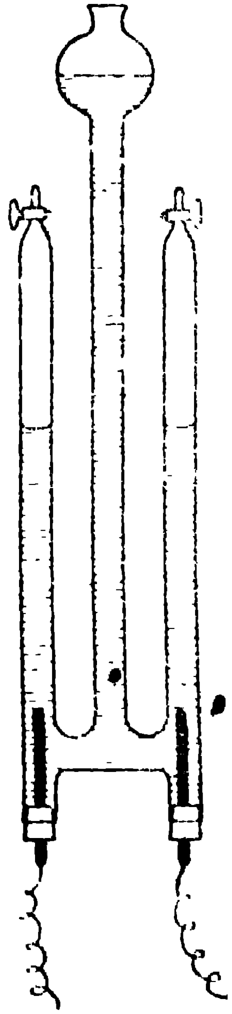

FIG. 42.

151. Synthetical proof of the Composition of Hydrogen Chloride.—The composition of hydrogen chloride may be conveniently investigated synthetically by means of the following experiment:—

Exp. 124.—Hydrochloric acid is electrolysed in the vessel A, Fig. 43 (using gas carbon electrodes), and when the liquid is saturated with chlorine a stout glass tube B, provided with a stopcock at each end, is attached to the delivery tube of A. The other end of B is connected with a bottle containing fragments of pumice stone moistened with caustic soda solution to absorb the chlorine as it escapes. The stopcocks are opened and the mixture of hydrogen and chlorine in equal volumes generated in A is passed through B for some time so that all the air is driven out.* The stopcocks are then closed and the tube disconnected.

On opening one of the stopcocks under a solution of potassium iodide the chlorine reacts with the KI, liberating iodine, and if the experiment has been conducted properly the liquid will rise just half-way up the tube, showing that the chlorine and hydrogen are present in equal volumes. The tube is now cleaned out and again filled with the electrolytic mixture of hydrogen and chlorine. The stopcocks are again closed and the tube is disconnected and exposed to the action of the rays from burning magnesium wire (the face should be protected by a thick sheet of glass to avoid accident in case the tube explodes). The gases combine with explosion. The tube is allowed to become quite cold and one of the stopcocks is then opened under mercury. No gas escapes and the mercury does not rise in the tube, showing that the volume of hydrochloric acid

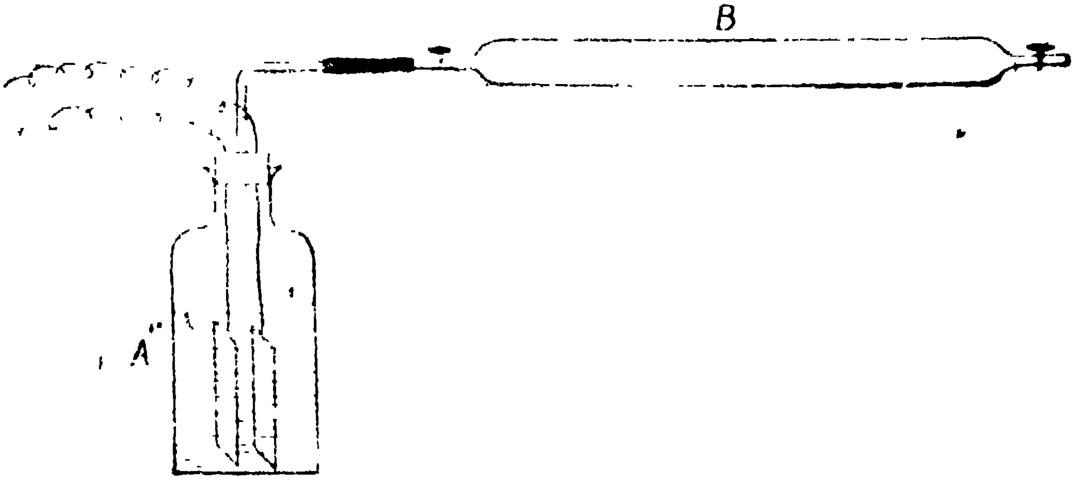

FIG. 43.

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* This must be done in the dark to prevent combination of the gases.

is exactly the same as that of the mixed gases from which it was formed. The stopcock is now closed and opened again under water; the water rushes up and fills the whole tube, the hydrogen chloride formed dissolving completely. This shows that the whole of the gases have combined to form hydrogen chloride. We thus arrive at the same composition for hydrogen chloride by synthesis as by analysis.

152. **Liquid Hydrogen Chloride.**—Hydrogen chloride condenses to a colourless liquid under a pressure of 40 atmospheres at 10° C.; the liquid boils under ordinary pressure at – 83·7° C. Liquid hydrogen chloride is without action on most metals, *e.g.* magnesium and zinc, nor does it act on metallic oxides, such as lime, or on anhydrous carbonates; it is therefore an inactive substance.

153. **Preparation of Aqueous Hydrochloric Acid.**—A solution of hydrogen chloride in water, commonly called hydrochloric acid (also known as "spirits of salts" and "muriatic acid"), may be conveniently prepared in the following manner:—

Exp. 125.—Generate hydrogen chloride in the flask A (Fig. 44), as described in Exp. 117, and pass the gas through an *empty* wash-bottle B, arranging so that the delivery tube of A reaches just below the cork of B. Lead the gas away by a delivery tube which reaches to the bottom of B and is connected by rubber tubing with a wider tube dipping in a beaker of water. The hydrogen chloride is absorbed by the water, and if the process is continued long enough the solution finally becomes saturated, when it contains from 40–45 % of HCl.

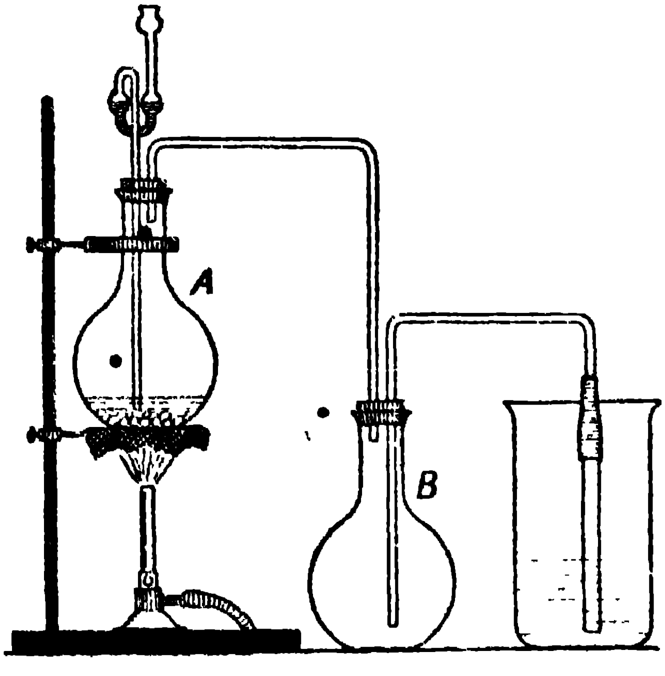

FIG. 44.

The object of the empty wash-bottle is to guard against any accident owing to a sudden cessation in the evolution of the gas which, owing to the great solubility of hydrogen chloride, would result in a reduction of pressure in the apparatus and consequent "sucking back" of the liquid in the beaker. If no wash-bottle were present the liquid would be sucked back into the generating flask, but with the arrangement described it merely passes into the empty wash-bottle. Further, by arranging the delivery tubes in the wash-bottle as shown, it is impossible for the liquid to pass back out of the wash-bottle into the generating flask, even if it is all sucked out of the beaker into the wash-bottle; all that will happen if the gas in the apparatus is still under reduced pressure will be that air will be drawn in through the delivery tube in the beaker, and will bubble through the liquid now present in B, and mix with the hydrochloric acid above this liquid till the pressure is atmospheric.

154. **Properties of Aqueous Hydrochloric Acid.**—Hydrochloric acid is a strongly acid liquid turning blue litmus a bright red; it is very corrosive, being much more active than the gas.

Action on Metals.—Many metals are attacked by hydrochloric acid, some readily by the dilute acid, others only by the hot concentrated acid. In all cases the products are a chloride of the metal and hydrogen. The following table gives a *résumé* of the action of the acid on a number of common metals under different conditions.

Metal.	Cold dilute HCl.	Hot conc. HCl.
Zinc	Dissolves readily	Dissolves readily
Magnesium	,, ,,	,, ,,
Iron	,, ,,	,, ,,
Aluminium	,, rather slowly	,, ,,
Tin	,, slowly	,, ,,
Copper	Insoluble*	,, slowly
Lead	,,	,, very slowly
Mercury	,,	Insoluble
Silver	,,	,,
Gold	,,	,,
Platinum	,,	,,

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* Copper is slowly attacked by dilute hydrochloric acid *in the presence of air*; the same remark applies to lead.

155. Chlorides.—The chlorides of the metals may be produced by the direct union of the metals with chlorine, or by the action of hydrochloric acid on the metals (in some cases) or on their oxides, hydroxides or carbonates. Zinc chloride, $ZnCl_2$, for instance, may be produced by any of these methods as shown in the following equations:—

$$\begin{array}{llll}
Zn & + \ Cl_2 & = ZnCl_2. & \\
Zn & + \ 2\,HCl & = ZnCl_2 + & H_2. \\
ZnO & + \ 2\,HCl & = ZnCl_2 + & H_2O. \\
Zn(OH)_2 & + \ 2\,HCl & = ZnCl_2 + & 2\,H_2O. \\
ZnCO_3 & + \ 2\,HCl & = ZnCl_2 + & H_2O + CO_2.
\end{array}$$

When a metal forms an *insoluble* chloride a special method of preparation is applicable, viz. the addition of a solution of a soluble chloride to a solution of soluble salt of the metal; double decomposition takes place, the insoluble chloride being precipitated. Silver chloride is, for example, precipitated when a solution of silver nitrate, $AgNO_3$, is added to a solution of calcium chloride, $CaCl_2$.

$$CaCl_2 + 2\,AgNO_3 = \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + \underset{\text{Silver chloride.}}{2\,AgCl.}$$

Most metallic chlorides are easily soluble in water; the only insoluble ones are mercurous chloride (calomel), $HgCl$, cuprous chloride, Cu_2Cl_2, lead chloride, $PbCl_2$ (which is sparingly soluble in cold water and readily in hot) and aurous chloride, $AuCl$, in addition to silver chloride already referred to.

156. Action of Heat on Hydrochloric Acid.—When a strong solution of hydrochloric acid is distilled it at first loses hydrochloric acid much faster than water, *i.e.* it becomes weaker. This goes on till the percentage of HCl is 20·24, when the liquid distils over unchanged in composition. Similarly, if a solution containing less than 20·24 per cent. of hydrochloric acid is distilled it loses water faster than HCl till the percentage of HCl is 20·24, when the liquid again distils unchanged. The boiling-point of hydrochloric acid of this particular strength is 110° C. It must be noted that the acid which distils unchanged only has the composition and boiling-point stated when the *pressure is normal;* for any other pressure, the composition and boiling-point of the liquid which distils unchanged have different values, which, however, are constant for each particular pressure.

157. **Manufacture of Hydrochloric Acid.**—Hydrochloric acid is manufactured in enormous quantities as a by-product in the conversion of common salt into salt-cake (sodium sulphate, Na_2SO_4) by the action of strong sulphuric acid. The first part of the process is performed at a gentle heat and the reaction is the same as that given in § 148. The mixture is then heated to a *much higher* temperature, when the acid sodium sulphate reacts with another molecule of sodium chloride, producing normal sodium sulphate and hydrochloric acid according to the equation—

$$\mathrm{NaCl} + \underset{\substack{\text{Acid sodium}\\ \text{sulphate.}}}{\mathrm{NaHSO_4}} = \underset{\substack{\text{Normal sodium}\\ \text{sulphate.}}}{\mathrm{Na_2SO_4}} + \mathrm{HCl}.$$

The gas is passed up stone towers filled with lumps of coke, over which a slow stream of water flows; the hydrochloric acid is absorbed, and the aqueous solution runs away from the bottom of the tower into suitable receivers.

Impurities in the Commercial Acid.—The chief impurities in commercial hydrochloric acid are ferric chloride, free chlorine, sulphuric acid, arsenious chloride, and sulphurous acid. The ferric chloride is the principal cause of the yellow colour usually noticeable in the commercial acid.

158. **Uses of Hydrochloric Acid.**—The most important use of hydrochloric acid is in the manufacture of chlorine. It is also used in dyeing and calico printing, in obtaining phosphates from bones, and in manufacturing colours. Its employment in the manufacture of metallic chlorides is also of importance, and it is very extensively used in chemical laboratories for a variety of purposes.

HYDROGEN BROMIDE OR HYDROBROMIC ACID, HBr.

* 159. **Preparation.**—Hydrogen bromide cannot conveniently be prepared from potassium or sodium bromide in the same way that hydrogen chloride is prepared from common salt, because some of the product undergoes a secondary reaction with sulphuric acid, reducing it to sulphurous acid with liberation of free bromine.

$$(1)\quad KBr + H_2SO_4 = KHSO_4 + HBr.$$
$$(2)\quad 2\ HBr + H_2SO_4 = Br_2 + SO_2 + 2\ H_2O.$$

This reducing action is a result of the instability of hydrogen bromide, which readily splits up into free hydrogen and bromine, the nascent hydrogen so produced then attacking the sulphuric acid thus—

$$2\ HBr = \underset{\text{Nascent.}}{2\ H} + Br_2.$$
$$2\ H + H_2SO_4 = 2\ H_2O + SO_2.$$

These two equations when combined give equation (2) above.

If, instead of sulphuric acid, an acid such as phosphoric acid, which is not so easily reduced, is employed, then the preparation can be carried on just as for hydrogen chloride.

The best method of preparation is to drop bromine on to a mixture of amorphous phosphorus and water, when the following reactions take place :—

$$P_4 + 16\ H_2O + 10\ Br_2 = \underset{\text{Phosphoric acid.}}{4\ H_3PO_4} + \underset{\text{Hydrogen bromide.}}{20\ HBr.}$$
$$P_4 + 12\ H_2O + 6\ Br_2 = \underset{\text{Phosphorous acid.}}{4\ H_3PO_3} + 12\ HBr.$$

The particular reaction which preponderates depends on the relative quantities of phosphorus and bromine used. It may be supposed that these reactions take place in two stages, phosphorus and bromine first uniting to form phosphorus pentabromide (PBr_5) and phosphorus tribromide (PBr_3), these compounds being immediately decomposed by water, thus—

$$P_4 + 10\ Br_2 = 4\ PBr_5.$$
$$P_4 + 6\ Br_2 = 4\ PBr_3.$$

$$PBr_5 + 4\,H_2O \quad H_3PO_4 + 5\,HBr.$$
$$PBr_3 + 3\,H_2O \quad H_3PO_3 + 3\,HBr.$$

The experiment is carried out as follows:—

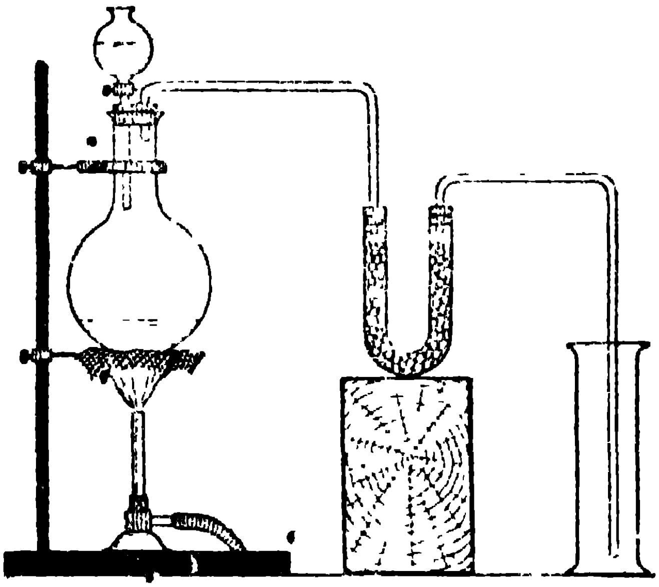

Fig. 45.

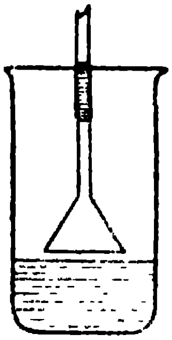

Fig. 46.

A mixture of one part of amorphous phosphorus and ten parts of water is introduced into a flask provided with a dropping funnel and delivery tube, as shown in Fig. 45. Ten parts of bromine are introduced into the funnel, and are *gradually* run into the flask; this is then *gently* warmed, and the hydrogen bromide is passed through a U-tube containing lumps of amorphous phosphorus to remove bromine, the gas being collected by downward displacement or over mercury. Like hydrogen chloride, it cannot be collected over water, owing to its great solubility. If an aqueous solution of the gas is required, the delivery tube from the U-tube in Fig. 45 should be connected with a wash-bottle and beaker of water as shown in Fig. 44. An even more convenient method of absorbing the gas (which can be used for any very soluble gas) is to connect the delivery tube from the U-tube with a funnel which reaches to *just above*[*] the surface of some water in a beaker as shown in Fig. 46. The hydrogen bromide is absorbed as fast as it reaches the water, and practically none of it escapes.

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[*] A variation of the method is to have the rim of the funnel *just below* the surface of the water. If the liquid "sucks back" its level in the beaker soon falls below the rim of the funnel, after which no more liquid can leave the beaker.

Another simple method of preparing a solution of the gas is to pass sulphuretted hydrogen into bromine water, when the following change takes place:—

$$2\ H_2S + 5\ Br_2 + 4\ H_2O = 10\ HBr + H_2SO_4 + S.$$

The precipitate of sulphur is filtered off and the liquid distilled, when hydrobromic acid passes over and sulphuric acid remains behind.

* 160. **Properties.**—Hydrogen bromide is a heavy colourless gas which, like hydrogen chloride, fumes in moist air, and has an irritating action on the mucous membrane. As already stated it is very soluble in water, producing a strongly acid solution which is very similar in properties to hydrochloric acid.

On distilling hydrobromic acid at normal pressure it loses either water or acid, according as the solution contains less or more than 48·17 per cent. of HBr. The liquid of this composition distils over unchanged at 126° C. If the pressure is not normal there is a corresponding change in the composition and boiling-point of the liquid which distils unchanged.

Hydrogen bromide is incombustible, and is a non-supporter of combustion. It is immediately attacked by chlorine with liberation of free bromine and formation of hydrogen chloride—

$$2\ HBr + Cl_2 = 2\ HCl + Br_2.$$

Potassium, on the other hand, immediately liberates free hydrogen from hydrogen bromide, and forms potassium bromide—

$$2\ HBr + 2\ K = 2\ KBr + H_2.$$

* 161. **Bromides.**—The general methods of preparation of metallic bromides are similar to those given for metallic chlorides. Most metallic bromides are readily soluble in water, the only common insoluble ones being silver bromide

(AgBr), mercurous bromide (HgBr), and lead bromide ($PbBr_2$), the last being sparingly soluble in cold water, but readily in hot water.

HYDROGEN IODIDE OR HYDRIODIC ACID, HI.

*162. **Preparation.**—Hydrogen iodide cannot be prepared by the action of sulphuric acid on potassium or sodium iodide for a reason similar to that given in the case of hydrogen bromide; hydrogen iodide is, in fact, much more unstable than hydrogen bromide, and the reaction goes almost entirely in accordance with the equation—

$$3\,H_2SO_4 + 2\,KI = 2\,KHSO_4 + SO_2 + 2\,H_2O + I_2.$$

If phosphoric acid is used, however, instead of sulphuric acid, hydrogen iodide is obtained free from iodine just as hydrogen bromide could be obtained free from bromine. Hydrogen iodide is best prepared by a method similar to that used for hydrogen bromide, namely, by the mutual interaction of phosphorus, iodine and water. The apparatus used is that shown in Fig 45; since iodine is a solid it cannot be run in from a stoppered funnel as bromine is; instead, the iodine and amorphous phosphorus are mixed in the flask, and water is slowly run in from the funnel. Hydrogen iodide is evolved without heating, and, after passing through the U-tube containing amorphous phosphorus which removes iodine vapour, is collected by downward displacement or over mercury. When all the water has been added and the evolution of gas becomes slow the flask may be gently warmed. The reaction which takes place is thus represented—

$$P_4 + 10\,I_2 + 16\,H_2O = 4\,H_3PO_4 + 20\,HI.$$

If an aqueous solution of the gas (called hydriodic acid) is required, the absorption may be carried out by one of the methods described for HBr, as HI is also very soluble in water.

Another convenient method for the preparation of hydriodic acid is to pass sulphuretted hydrogen through water containing iodine in suspension, when the following change takes place:—

$$SH_2 + I_2 = 2\,HI + S.$$

The hydriodic acid is separated from the precipitate of sulphur by distillation.

*163. **Properties.**—Hydrogen iodide is a very heavy colourless gas which, like the other halogen hydrides, fumes strongly in moist air and has a very irritating action on the mucous membrane. Its great solubility in water has already been referred to; the aqueous solution has strongly acid properties just like the solution of the other halogen hydrides. The behaviour of the solution on distillation is exactly similar to that of hydrochloric acid and hydrobromic acid; the liquid which distils unchanged at normal pressure contains 57·7 per cent. of hydrogen iodide and boils at 127° C., but at other pressures the composition and boiling-point have different values. Hydrogen iodide is easily condensed to a liquid, a pressure of four atmospheres at 0° C. sufficing to bring this about; the liquid boils at −34·1° C. under normal pressure. Hydrogen iodide does not burn nor does it support combustion. As already pointed out, it is an unstable substance; thus on exposing the gas to sunlight it slowly undergoes decomposition into its elements, and on heating it breaks up much more quickly. Also the aqueous solution gradually turns brown in sunlight owing to separation of free iodine. On account of its instability and consequent tendency to produce nascent hydrogen, hydriodic acid is a powerful reducing agent, and is much used as such in organic chemistry; we have already had occasion to notice its reducing action on strong sulphuric acid.

Hydrogen iodide, both in the gaseous state and in aqueous solution, is at once decomposed by chlorine or bromine with liberation of free iodine—

$$Br_2 + 2\,HI = 2\,HBr + I_2.$$

* 164. **Iodides.**—The iodides of the metals are produced by methods similar to those given for chlorides and bromides. The majority of the iodides dissolve easily in water, the chief insoluble ones being silver iodide (AgI), mercurous iodide (HgI), mercuric iodide (HgI_2), cuprous iodide (Cu_2I_2), and lead iodide (PbI_2), the last being sparingly soluble in cold water and readily in hot.

* 165. **Tests for the Halogen Acids and their Salts.**

(1) A solution of silver nitrate, $AgNO_3$, when added to a solution of a halogen acid or haloid salt, gives with

Hydrochloric acid, a white curdy precipitate of silver chloride, AgCl, soluble in ammonia, insoluble in nitric acid.

Hydrobromic acid, a pale yellow precipitate of silver bromide, AgBr, soluble in strong ammonia, insoluble in nitric acid.

Hydriodic acid, a yellow precipitate of silver iodide, AgI, insoluble in ammonia and nitric acid.

(2) Free HCl, HBr, or HI, heated with manganese dioxide, or their salts, heated with manganese dioxide and sulphuric acid, evolve chlorine, bromine and iodine respectively, and these elements are easily recognised by their colour, smell and bleaching action.

(3) Chlorine water (which must not be in excess) added to a bromide or iodide liberates bromine or iodine, and on shaking the liquid with carbon bisulphide, the bromine imparts to it a red colour and the iodine a violet colour.

QUESTIONS.—CHAPTER XV.

1. How would you prepare *pure dry* hydrogen chloride? Describe experiments which illustrate the chief properties of the gas.
2. State the changes which take place when very concentrated and very dilute hydrochloric acid are respectively boiled for some time in an open vessel.

3. On what evidence do we accept HCl as expressing the composition of hydrochloric acid gas?
4. Compare the properties of liquid hydrogen chloride with those of an aqueous solution of the gas.
5. What is the action (if any) of (*a*) cold dilute, (*b*) hot strong hydrochloric acid on the following metals: (1) zinc, (2) aluminium, (3) gold, (4) lead, (5) copper, (6) tin?
6. State briefly the general methods of preparing metallic chlorides, giving equations.
7. How is hydrochloric acid manufactured? What are the chief impurities in the commercial acid?
8. Enumerate the chief uses of hydrochloric acid.

*9. Describe in detail the laboratory method of preparing an aqueous solution of hydrobromic acid.

*10 Describe a method of preparing gaseous hydriodic acid. In what respects do hydriodic acid and hydrochloric acid resemble each other, and in what respects do they differ?

CHAPTER XVI.

NITROGEN—THE ATMOSPHERE—AMMONIA.

NITROGEN, N_2.

166. NITROGEN is the first member of a group of elements, nitrogen, phosphorus, arsenic, antimony and bismuth, which either in themselves or their compounds exhibit considerable analogy to one another. The first two members only are usually classed with the non-metals.

The elements forming this group show a transition in physical properties as the atomic weight increases, nitrogen being gaseous at the ordinary temperature, whilst phosphorus is solid but easily vaporised, the other members being more difficult to volatilise.

Speaking more particularly with regard to nitrogen and phosphorus, it will be seen by a reference to the following pages that they resemble one another:—

(1) In forming hydrides of similar composition NH_3, PH_3, both of which combine directly with haloid acids yielding the ammonium and phosphonium salts.

(2) In forming a characteristic series of oxides some of which yield powerful acids.

167. **Occurrence.**—Nitrogen occurs mixed with oxygen in the atmosphere, of which it forms nearly four-fifths the volume.

Although it does not enter to any large extent into the composition of animal and vegetable tissues, it is, notwithstanding, a very constant and essential constituent of such tissues. The nitrogen of plants is obtained chiefly through the medium of the soil, in which small quantities of nitric acid, nitrates and ammonium salts always occur. Animals cannot assimilate nitrogen directly, and derive their supply from the plants.

168. **Preparation.**—We have seen in Experiments 18 and 19 that air may be deprived of its oxygen by means of iron or phosphorus. The most convenient method of bringing this about in practice is to pass air over heated copper contained in a hard glass tube. The nitrogen so obtained is not pure, for air contains a number of other inert gases, chiefly argon, in addition to nitrogen (see § 179). The best method of preparing pure nitrogen is to heat a solution of ammonium nitrite—

$$NH_4NO_2 = N_2 + 2\ H_2O.$$

In practice a mixture of ammonium chloride, NH_4Cl, and sodium nitrite, $NaNO_2$, is used instead of ammonium nitrite, since both NH_4Cl and $NaNO_2$ are common salts, whereas NH_4NO_2 is an unstable compound. We may suppose that the NH_4Cl and $NaNO_2$ undergo double decomposition with formation of NH_4NO_2 and $NaCl$, and that the ammonium nitrite is then decomposed according to the equation given above.

Exp. 126.—Introduce about 15 grammes of sodium nitrite and 10 grammes of ammonium chloride into a small flask, and add about 100 c.c. of water. Fit the flask with a cork carrying a delivery tube. Warm gently and collect the nitrogen over water at the pneumatic trough.

If the nitrogen is required dry, it should be passed through a sulphuric acid wash-bottle and collected over mercury.

Another method of preparation is to heat ammonium bichromate $(NH_4)_2Cr_2O_7$.

$$(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4\ H_2O.$$

Instead of ammonium bichromate, it is more convenient to use a mixture of ammonium chloride and potassium bichromate, which serves the same purpose. Nitrogen can also be obtained by the action of chlorine on a concentrated solution of ammonia, taking care to keep a large excess of ammonia present throughout the experiment, thus preventing the formation of the explosive chloride of nitrogen—

$$8\ NH_3 + 3\ Cl_2 = N_2 + 6\ NH_4Cl.$$

This reaction may be represented in two stages—

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ HCl.$$
$$6\ NH_3 + 6\ HCl = 6\ NH_4Cl.$$

169. **Properties of Nitrogen.**—Nitrogen is a colourless, tasteless gas, which is unable to support life or combustion. Nitrogen does not combine with oxygen under ordinary conditions; but it may be made to do so by means of an alternating current of electricity, when nitrogen peroxide is formed. It is somewhat lighter than air, and condenses to the liquid form at − 193° C.; it is slightly soluble in water, less so than oxygen (see § 107).

The chief characteristic of nitrogen is its inertness, but at the same time there are some elements with which it readily combines directly, *e. g.* magnesium, boron, titanium and tungsten; the last two do not require heating if they are in a finely-divided state. Nitrogen also combines directly with barium, strontium, lithium, aluminium, silicon, carbon and hydrogen.

170. **The Atmosphere.**—The gaseous envelope which surrounds the earth is chiefly composed of nitrogen and oxygen. With these are associated argon, water vapour, carbon dioxide, ammonia, and other gases, the amounts of which vary according to circumstances. From whatever locality the air has been obtained, the relative proportions of nitrogen and oxygen exhibit only slight variations, as the following results show:—

Percentage of Oxygen by Volume.

72	analyses in different parts of Europe (mean)	20·95
17	„ „ the Polar Seas „	20·90
3	„ at elevation of 15,000 ft. or over „	20·94.

171. Determination of the Composition of the Atmosphere by Volume.—A rough method of determining the volumetric composition of the atmosphere has already been described in Exp. 19. A better method is to explode a known volume of air with about twice its volume of hydrogen in a eudiometer; two volumes of hydrogen combine with one volume of oxygen to form water vapour, which condenses, and thus *one-third* the diminution in volume represents the volume of oxygen present. This method is not quite accurate, because some of the nitrogen and oxygen combine to form nitrogen peroxide, which

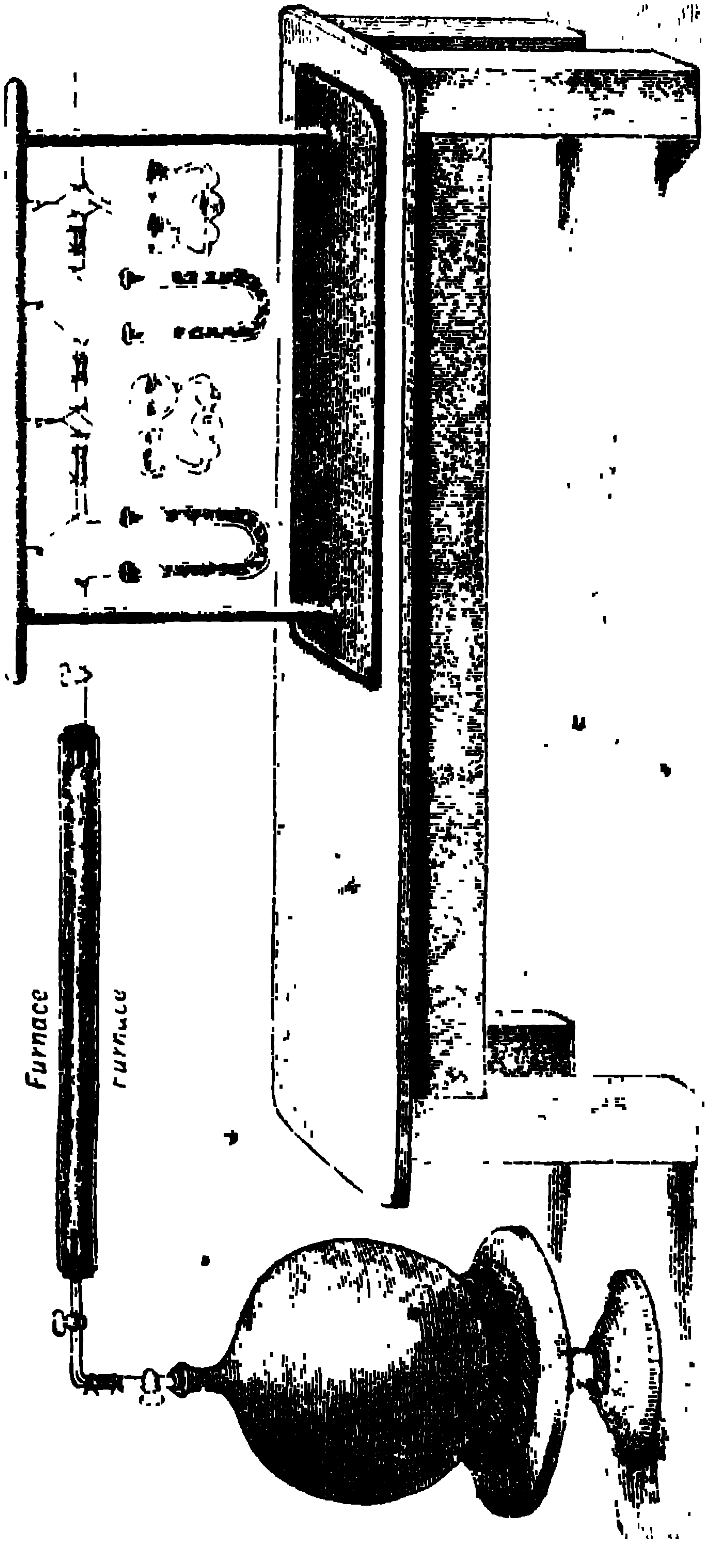

FIG. 47.

dissolves in the water produced with formation of nitric and nitrous acids.

172. Determination of the Composition of the Atmosphere by Weight.—This may be ascertained by passing the air over red-hot copper, with which the oxygen combines, as in the experiment just described.

The air is previously freed from carbon dioxide and moisture by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig. 47; it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air pump, the stopcock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed and weighed. The copper having been heated to redness, the stop-cock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen and argon pass into the globe. After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen and argon*. The tube is also weighed again, and the increase there shows *the weight of the oxygen*, together with a little nitrogen and argon which remain in the tube. On exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen and argon. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen and argon	76·995
Oxygen	23·005.

173. Water Vapour in Air.—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated.

The average amount is somewhat under 1 per cent. by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dew-point (see text-books on physics), or by passing a known volume of air over calcium chloride contained in U-tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be estimated by the fact that 1 cubic mile of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than $\frac{1}{10}$ of the possible amount.

174. **Carbon Dioxide in Air.**—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of CO_2 in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish; the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—

$$\underset{\text{Calcium hydroxide.}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{Calcium carbonate.}}{CaCO_3} + H_2O.$$

Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A known volume of a solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralise a known volume of the original baryta water, and that required to neutralise the liquid which remains after partial neutralisation as already described, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

175. **Other impurities in Air.**—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acid ; ozone is also probably produced under such circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found.

The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the neighbourhood of the sea contains much more sodium chloride than is usual.

176. **The relation of Animal and Plant Life to Air.**—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent. of carbon dioxide, that is, over one hundred times as much as normal air.

The agencies at work in producing carbon dioxide are—

(1) Respiration of animals and plants ; (2) Combustion of fuel ; (3) Decay of organic matter ; (4) Subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly

get more and more charged with carbon dioxide, and the percentage of oxygen would diminish.

There are, however, processes constantly in operation which act in the opposite direction.

(1) In the process of assimilation in plants, the green colouring matter (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water.

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime, when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on.

177. **Is Air a compound or a mixture of Nitrogen and Oxygen?**—We have seen that a chemical compound shows the following characters:—

(1) It possesses a *definite* composition (see § 46).

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights. This follows from the Atomic Theory—see Chap. VII.

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constituent elements being more or less completely concealed (see § 45).

(4) When combination takes place, heat is usually evolved.

(5) When gases combine to form a gaseous compound there is generally a contraction in volume, thus—

2 vols. of hydrogen + 1 vol. of oxygen form 2 vols. of water vapour.

3 vols. of hydrogen + 1 vol. of nitrogen form 2 vols. of ammonia.

(6) The simple solution of a gas in water does not affect its chemical composition; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown. Of the 76·995 per cent. of nitrogen and argon present in air 0·937 per cent. is argon, so that the percentage of nitrogen is 76·995−0·937 = 76·058. We have therefore—

$$\text{Nitrogen } \frac{76{\cdot}058}{14} = 5{\cdot}433\,;$$

$$\text{Oxygen } \frac{23{\cdot}005}{15{\cdot}96} = 1{\cdot}441\,;$$

$$\text{And } 5{\cdot}433 : 1{\cdot}441 :: 3{\cdot}77 : 1.$$

That is, to be even approximately in agreement with the results of analysis we should have to assume a compound $N_{15}O_4$ (3·77 : 1 = 15·08 : 4). The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

(6) We have seen (§ 109) that when air is shaken up with water, a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that whilst in the air originally taken, one volume of oxygen is associated with approximately four

volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen.

The following additional reasons may be mentioned:—

(7) The constituents of air can be partly separated by diffusion, for, owing to the difference in density of nitrogen and oxygen, they do not diffuse through a porous membrane at equal rates (see § 55) ; if the gases were combined the compound would diffuse *as a whole*.

(8) When liquid air boils the nitrogen distils off before the oxygen and argon.

(9) The refractive index of air is the mean of those of oxygen and nitrogen; in the case of compounds the value is invariably found to be either above or below the mean of the values for the constituents.

178. **Fogs** are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air fogs cannot form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five times the normal amount.

ARGON AND ITS COMPANIONS.

179. In the year 1894 Lord Rayleigh noticed that the density of nitrogen obtained from the air was about 0·4 per cent. greater than that of nitrogen prepared by chemical methods. The only explanation which could be offered was that air contained a small quantity of another inert gas in addition to nitrogen, and that this gas had a greater density than nitrogen. Ramsay took up the question and succeeded in isolating this gas; he passed air freed from carbon dioxide and water vapour over red-hot copper which removed the oxygen, and then over red-hot

magnesium* which removed the nitrogen. The residue amounted to about 1 per cent. of the air used, and consisted of a very inert gas which Ramsay could not decompose or cause to combine with any known substance. He came to the conclusion that the new gas was an *element*, and on account of its inertness he called it *argon*. Argon has a molecular weight of 40 as determined from its density, and its molecule has been shown to contain one atom; the atomic weight is therefore also 40. Argon liquefies at – 187° C. and solidifies at – 189·5° C.

More recently Ramsay has discovered several other new elementary gases in the atmosphere, namely, *helium*, *neon*, *krypton* and *xenon*. He fractionally distilled large quantities of liquid air, and from the lowest boiling portions isolated two elements, helium and neon. From the portions boiling at a higher temperature than oxygen, nitrogen and argon, he isolated krypton and xenon. These elements are only present in exceedingly small quantities in the atmosphere; they are all very inert like argon and have not, up to the present, been induced to combine with any known substance.

As in the case of argon, so with these other elements the molecule contains one atom.

Helium has been found in some uranium ores and in certain springs as well as in the atmosphere. Helium is the most difficult of all gases to liquefy, its boiling-point being very near the absolute zero of temperature. Its atomic weight is 4.

The atomic weights of neon, krypton and xenon are respectively 20, 81·75 and 128.

AMMONIA, NH_3.

180. **Occurrence.**—Ammonia or its compounds exist in small quantities in air and in natural waters, being produced either from the nitrogen present in the air, or by the action of bacteria from refuse matters in the soil.

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* It has recently been found better to mix the magnesium with quicklime.

181. **Preparation.**—Whenever animal or vegetable products containing nitrogen are strongly heated in closed retorts (air being excluded), and especially when they are heated with lime or other alkalies, ammonia is given off.

In this way large quantities of ammonia are obtained during the distillation of coal (which contains about 1½ per cent. of nitrogen), the coal gas being cooled and then washed, by which means any ammonia is separated and obtained in solution. The further distillation of the liquid so obtained with lime sets free the ammonia, which, if passed into aqueous hydrochloric acid, forms ammonium chloride or sal ammoniac—

$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl.}$$

In the laboratory ammonia is usually prepared by heating a mixture of ammonium chloride and slaked lime, $Ca(OH)_2$—

$$2\,NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\,NH_3 + 2\,H_2O.$$

Exp. 127.—Weigh out about 10 grammes of ammonium chloride and 20 grammes of dry slaked lime and grind them up in a mortar till they are in a state of a fine powder and intimately mixed. Introduce the mixture into a small dry round-bottomed flask, and connect this with a U-tube containing lumps of quicklime or caustic soda, as shown in Fig. 48. Now heat the flask gently when ammonia will be evolved, and after being dried by the lime or caustic soda in the U-tube may be collected by upward displacement, being much lighter than air. Ammonia can also be collected over mercury, but not over water in which it is very soluble.

The ordinary drying agents for gases—sulphuric acid, calcium chloride and phosphorus pentoxide—cannot be used in the case of ammonia, since it combines readily with them.

182. **Properties**—Ammonia is a colourless gas, having a very pungent but not disagreeable odour if diluted with much air; in the pure condition it is injurious when breathed in quantity. At −34° C. under ordinary pressure, and at 0° C. under a pressure of seven atmospheres, dry ammonia condenses to the liquid form (see below, Carré's apparatus).

Exp. 128.—Fill a litre flask by displacement with dry ammonia, and show its solubility in the same way as already described (Exp. 118).

Water at 0° C. dissolves 1,050 times its volume of the gas, and at 15° C. 727 volumes. The aqueous solution is lighter than water, and in its most concentrated form has the specific gravity 0·884; it contains 36 per cent. by weight of the gas. The gas may be entirely expelled by boiling the solution.

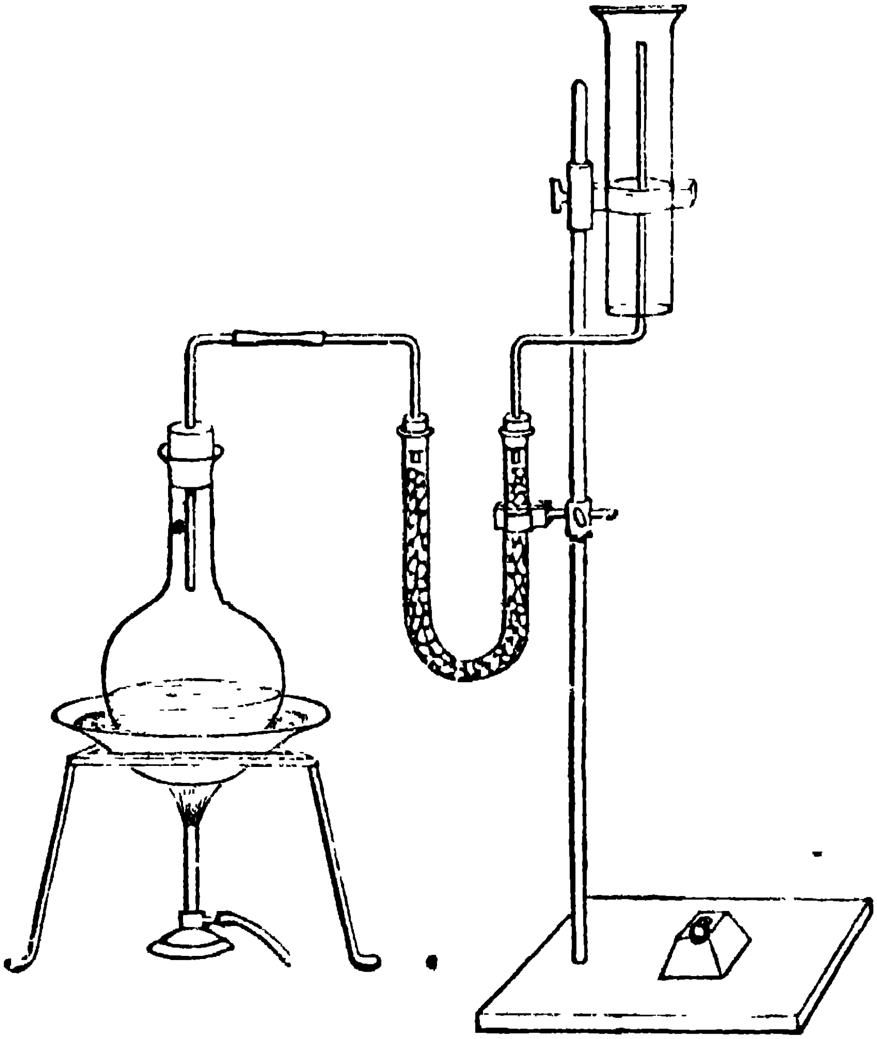

FIG. 48.

Ammonia neither burns readily in air nor supports combustion, but a mixture of warm ammonia and oxygen burns with a greenish-yellow flame.

Exp. 129.—Gently warm a strong solution of ammonia in a wide-mouthed eight-ounce flask, and bubble oxygen gas through the solution at the same time. A mixture of ammonia and oxygen will pass out at the open mouth of the flask, and will burn when a light is applied to it.

Metallic oxides which are reduced in hydrogen also undergo reduction when heated in ammonia gas; the hydrogen of the ammonia combines with the oxygen of the oxide to form water, and nitrogen is set free.

183. **Ammonium Salts.**—Ammonia in presence of water is a strong alkali, and combines directly with acids to form ammonium salts; this can be well shown with hydrochloric acid gas.

Exp. 130.—Fill two similar jars by displacement with ammonia and hydrochloric acid gas respectively, and cover the mouth of each jar with a glass plate. Now bring them mouth to mouth and withdraw the glass plates. The gases as they come into contact will combine, forming a fine white powder which remains for some time diffused throughout the jars. This body is ammonium chloride, NH_4Cl—

$$\underset{\text{2 vols.}}{NH_3} + \underset{\text{2 vols.}}{HCl} = NH_4Cl.$$

Ammonium sulphate, $(NH_4)_2SO_4$, ammonium nitrate, NH_4NO_3, and other salts may be obtained by neutralising a solution of ammonia with the respective acids, and then evaporating to dryness on a water-bath.

The ammonium salts all contain the group of atoms NH_4, which in them plays the same part as an atom of a monovalent metal. NH_4 does not exist in the free state. Such a group of atoms, which enters into a series of compounds, is called a *compound radicle.* We have had an example of a compound radicle in the case of hydroxyl (OH). These two radicles combine together when ammonia gas dissolves in water, forming ammonium hydroxide, NH_4OH.

The ammonium salts strongly resemble the salts of potassium and sodium but differ from them in one important respect, namely, their behaviour towards heat. We shall study this property at some length.

When ammonium chloride is heated, it *apparently* sublimes unchanged, the vapour condensing again to ammonium chloride. It has been shown, however, that the vapour is not that of ammonium chloride, but is a mixture of ammonia and hydrochloric acid,* which recombine on cooling—

$$NH_4Cl = NH_3 + HCl.$$

This dissociation is proved by measurement of the vapour density, and, more directly, by partially separating the two gases by diffusion.

The ammonium salts of less volatile acids, *e.g.* sulphuric and phosphoric acids, are also dissociated by heat, but in this case the volatile ammonia comes off alone, leaving the acid behind—

$$(NH_4)_2SO_4 = 2\ NH_3 + H_2SO_4.$$

The ammonium salts of the oxyacids of nitrogen are not dissociated but decomposed by heat, giving either nitrogen and water, or nitrous oxide and water—

$$\begin{aligned} NH_4NO_2 &= N_2 + 2\ H_2O \\ NH_4NO_3 &= N_2O + 2\ H_2O. \end{aligned}$$

As already mentioned, ammonia combines directly with calcium chloride, the compound being represented by the formula $CaCl_2 \cdot 8\ NH_3$.

184. **Liquefaction of Ammonia by Pressure.**—If ammonia gas be generated in quantity, and the receiver into which it passes be a closed vessel much smaller than the volume of the gas generated, it will be compressed and ultimately condense by its own pressure to the liquid form. This is indeed the method of Faraday (see § 51), and a simple form of apparatus in which this principle is made use of is that of Carré (Fig. 49). It consists essentially of a strong iron cylinder containing concentrated ammonia solution, as shown at A in the figure; this communicates with a receiver B, of relatively small volume, by means of the tube C. When A is surrounded by hot water, ammonia gas is given off freely and accumulates in the apparatus in such quantity that it condenses in the receiver B, which has been surrounded by cold water.

---

* If however the ammonium chloride is *absolutely dry*, it volatilises without dissociation.

If we now reverse the arrangement and surround A with cold water, the liquid ammonia will boil very rapidly and pass back as gas into A, and this rapid transformation of liquid into gas will bring about a considerable depression of temperature in B. This vessel is provided with a space D, into which water may be introduced and frozen. By various applications of this principle, liquid ammonia is used on a large scale for obtaining low temperatures.

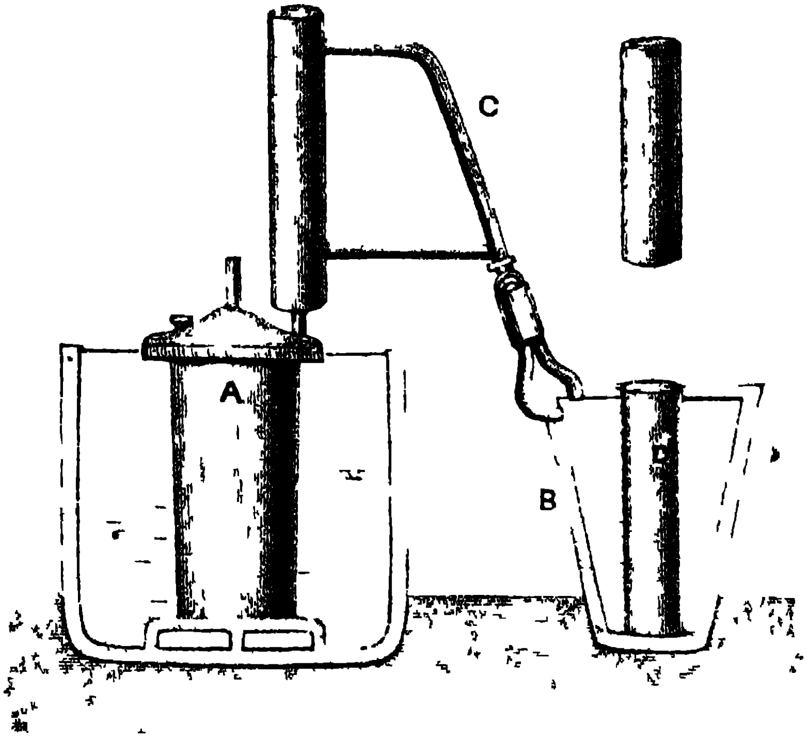

Fig. 49.

185. **Composition of Ammonia.**—The composition of ammonia may be determined by passing the gas through a red hot tube containing copper oxide. The hydrogen is transformed into water, which may be collected and weighed in the manner already described (§ 95), and the volume of nitrogen which passes forward may also be ascertained—

$$3\,CuO + 2\,NH_3 = 3\,Cu + 3\,H_2O + N_2.$$

The *volume* of hydrogen may be readily calculated from the weight of water obtained.

A second method depends on the fact that when electric sparks are passed through gaseous ammonia it is slowly decomposed into its constituents. Dry ammonia is passed into a eudiometer over mercury, and its volume accurately measured. The sparks are then passed until no further increase in volume occurs; the final volume will be found to be just *double* the original volume. If now excess of oxygen be passed into the eudiometer and the spark passed, the hydrogen will combine with it and form water, which condenses, leaving nitrogen and the *excess* of oxygen added, two-thirds the diminution being the volume of hydrogen. The volume of nitrogen is found by subtracting the volume of hydrogen calculated from this diminution, from the volume of nitrogen plus hydrogen obtained after the first sparking.

This method is not very accurate owing to the fact that some of the nitrogen combines with oxygen, forming oxides of nitrogen. By the electrolysis of ammonia it may however be shown that the volume of nitrogen it contains is one-third that of the hydrogen. The experiment is performed in the following manner. A saturated solution of common salt is prepared, and to this is added about one-tenth of its volume of strong ammonia. The solution is now introduced into a voltameter similar to that figured on page 193, but fitted with carbon electrodes and submitted to the action of the current from six Bunsen cells. Nitrogen collects in one tube and hydrogen in the other, and the volumes will be found to be in the proportion 1 : 3.

One of the most convenient methods of proving the volumetric composition of ammonia depends upon the fact that chlorine is capable of removing the hydrogen from it with liberation of free nitrogen, as we saw in § 168. A long glass tube closed at one end is divided into three equal parts by india-rubber bands. It is next filled with chlorine at the pneumatic trough by displacement of chlorine water, and when quite full the mouth is closed by a cork carrying a small dropping funnel; this is done *before* the tube is removed from the trough so as to prevent any chlorine escaping. The tube is now placed in an upright position and about 10 cubic centimetres of strong ammonia solution are introduced into the funnel. This solution is allowed to flow into the tube drop by drop: the first drop which enters reacts with the chlorine with formation of a yellowish-green flame, and as more ammonia enters dense clouds of ammonium chloride are produced. When all the ammonia has been run in, a little dilute hydrochloric acid is introduced through the funnel to combine with the excess of ammonia. The gas which now remains in the tube is nitrogen under reduced pressure. In order to bring it to atmospheric pressure the funnel is filled with dilute hydrochloric acid; a tube bent twice at right angles, with one long arm and one short arm, is also filled with dilute acid, and the short arm is attached to the funnel by rubber tubing, whilst the long arm is dipped into some more acid contained in a beaker (see Fig. 50). On now opening the tap hydrochloric acid is sucked into the tube until the pressure is the same as that of the atmosphere. It will then be found that the liquid reaches to the second india-rubber band, *i. e.* the nitrogen occupies one-third of the tube. Now hydrogen and chlorine unite in equal volumes to form hydrochloric acid, so that the volume of hydrogen extracted from ammonia by the chlorine in the tube would just fill the tube. This hydrogen was originally in combination with the nitrogen left in the tube, so that the relative volumes of hydrogen and nitrogen in ammonia are in the ratio 1 : 3.

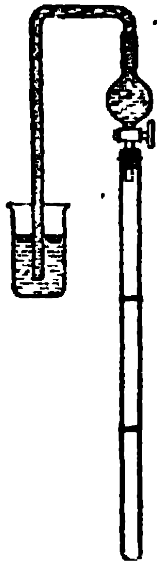
FIG. 50.

By combining with this result a knowledge of the density of ammonia we can completely prove its composition.

Since the volumes of nitrogen and hydrogen which combine to form ammonia are in the ratio 1 : 3, it follows by Avogadro's hypothesis that the number of molecules of nitrogen and hydrogen which combine are in the same ratio. But the molecules of these two elements each contain two atoms, and therefore—

$$\frac{\text{Number of atoms of nitrogen in ammonia}}{\text{Number of atoms of hydrogen in ammonia}} = \frac{1}{3}$$

The formula of ammonia is, therefore, NH_3 or N_2H_6 or N_3H_9, etc.

Now the relative density of ammonia is 8·5 ($H = 1$), and consequently its molecular weight is $8 \cdot 5 \times 2 = 17$.

Let us take first the simplest formula, viz. NH_3. Since atomic weight of $N = 14$ and atomic weight of $H = 1$ the molecular weight of NH_3 is $14 + 1 \times 3 = 17$. This agrees with the number obtained from the density, so that NH_3 is the correct formula.

186. **Tests for Ammonia.**—Ammonia may be recognised by its smell, action on litmus, and by giving dense white fumes of ammonium chloride when brought in contact with hydrochloric acid gas. With Nessler's solution ammonia gives a characteristic brownish coloration or precipitate, according to the amount of ammonia present.

All ammonium compounds give off ammonia when treated with lime or caustic potash.

QUESTIONS.—CHAPTER XVI.

1. Describe a method by which nitrogen may be obtained from air by removal of oxygen.
2. Give two methods for the preparation of nitrogen from ammonia or ammonium salts.
3. State the chief physical and chemical properties of nitrogen.
4. Describe a method of determining the composition of the atmosphere by volume.
5. How may the composition of the air by weight be determined?
6. A mixture of 25 c.c. of air and 50 c.c. of hydrogen is exploded in a eudiometer, and the volume of the residual gas is found to be 60·3 c.c.; find the percentage of oxygen in the air.
7. The percentage composition of air by weight being

76·058 nitrogen, 0·937 argon and 23·005 oxygen, find the composition by volume.

8. A litre of dry air is passed over heated copper and the increase in the weight of the copper found to be 0·297 gramme: find the percentage by weight of oxygen in the air. (1 litre of air weighs 1·293 gramme.)
9. How would you show that air contains carbon dioxide, and what means would you adopt for ascertaining the amount of carbon dioxide in air?
10. How do the following impurities originate in air:—carbon dioxide, sodium chloride, ammonia, sulphurous acid?
11 What agencies are at work which tend to remove such impurities as carbon dioxide and ammonia from the air?
12. In what respect does a *mixture* of two gases, such as nitrogen and oxygen, differ in its behaviour from a *compound* of the two gases when shaken up in contact with water?
13. What indications are usually shown that two gases which you have brought together have entered into combination?
14. What reasons are there for supposing that the nitrogen and oxygen in air are mixed, not chemically combined?
15. Write a short account of argon and the other elements recently discovered in the atmosphere.
16. Give a general method by which ammonia may be obtained from nitrogenous animal or vegetable substances.
17. How would you prepare and collect dry ammonia?
18. How can it be shown that ammonia contains hydrogen?
19. Explain what is meant by a *compound radicle.*
20. What experiments would you make to show that the composition of ammonia is rightly expressed by the formula NH_3?
21. Under what circumstances do nitrogen and hydrogen enter into combination, and under what circumstances is the compound so formed decomposed again without the intervention of chemical reagents?

CHAPTER XVII.

OXIDES AND OXYACIDS OF NITROGEN.

187. In the following table is given a list of the oxides and oxyacids of nitrogen :—

Nitrous oxide, N_2O.	Hyponitrous acid, $H_2N_2O_2$.
Nitric oxide, NO.	
Nitrogen trioxide or nitrous anhydride, N_2O_3.	Nitrous acid, HNO_2.
Nitrogen peroxide, N_2O_4.	
Nitrogen pentoxide or nitric anhydride, N_2O_5.	Nitric acid, HNO_3.

Occurrence.—The higher oxides are formed in small quantity when the electric discharge takes place in a mixture of nitrogen and oxygen. These oxides, or nitrous and nitric acid formed from them, therefore occur in the atmosphere and in rain water; waters contaminated by the drainage of surface soil, or by decaying nitrogenous organic matter, also contain similar products. In all such cases, owing to the difficulty of bringing about direct combination of nitrogen and oxygen, they are present in very minute quantities. Nitric acid or the nitrates being in all cases the source from which the oxides of nitrogen are derived, we shall treat these first.

NITRIC ACID, HNO_3.

188. **Preparation.**—Nitric acid, being a volatile acid, is expelled from nitrates by the action of less volatile acids, such as concentrated sulphuric acid (or silica), and this reaction is made use of in its preparation, nitrate of potash or soda being usually employed.

Exp. 131.—Introduce 20 grammes of potassium nitrate into a stoppered retort, and as much concentrated sulphuric acid as will just cover it. Apply a moderate heat, and presently the vapour of nitric acid will pass over and condense in the neck of the retort. The liquid may be collected in a small flask slipped over the mouth of the retort, and kept cool by means of a stream of cold water or a wet cloth. When about 10 c.c. have been distilled over, or so soon as whitish fumes of sulphuric acid begin to appear, the experiment should be stopped—

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

189. **Properties of the Acid.**—The pure acid is a colourless, fuming liquid, of specific gravity 1·53, boiling at 86° C. with partial decomposition into nitrogen peroxide, oxygen and water. It is highly corrosive, and by contact instantly stains the skin yellow, more prolonged exposure giving rise to serious wounds. Dry straw and woody fibre are charred or even set fire to by contact with it. It mixes with water in all proportions, and if the dilute solution be concentrated in air at atmospheric pressure it becomes stronger until 68 per cent. of acid is present; it then distils unchanged at 120·5° C. under normal pressure. Similarly, on distilling an acid stronger than this, it gradually becomes weaker till it contains 68 per cent. of HNO_3, when it passes over unchanged. If the pressure is not normal the composition and boiling-point of the acid which distils unchanged have different values, as in the case of the halogen acids.

As already stated, pure nitric acid decomposes to some extent at its boiling-point; at higher temperatures this decomposition takes place very readily, as may be illustrated by the following experiment:—

Exp. 132.—Support a clay pipe in the position shown in the diagram by means of a retort-stand and clamp (not shown). Heat the tube strongly at a spot about 9 inches from the bowl by means of a Bunsen burner, and then pour about 5 c.c. of strong nitric acid into the bowl. On reaching the heated part, decomposition takes place, and the weight of acid above pushes the gaseous products out through the stem of the pipe. The oxygen may be collected over water; the nitrogen peroxide being soluble goes into solution.

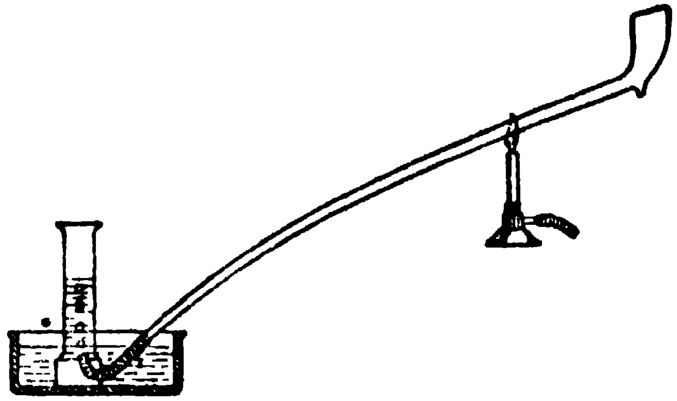

FIG. 51.

The equation representing the decomposition of nitric acid on heating is—

$$4\,HNO_3 = 2\,H_2O + 4\,NO_2 + O_2.$$

On account of the large percentage of oxygen which nitric acid contains (76 per cent.), and of the ease with which it parts with some of this oxygen, we should expect it to possess strong oxidising properties, and such is the case. Thus it readily transforms C, S, P and I into CO_2, H_2SO_4, H_3PO_4 and HIO_3 respectively, whilst turpentine when mixed with it inflames.

190. **Action on Metals.**—Most metals dissolve readily in nitric acid with evolution of red fumes, the nitrate of the metal, or in some cases the oxide, being formed. It is only rarely that free hydrogen is one of the products of the reaction. We may suppose that the first action of nitric acid on a metal is to convert it into the nitrate with liberation of *nascent* hydrogen, but the latter is immediately oxidised to water by a further quantity of nitric acid. Thus, taking the case of copper which reduces dilute nitric acid chiefly to nitric oxide, the two stages may be thus represented—

$$(1)\quad Cu + 2\,HNO_3 = Cu(NO_3)_2 + \underset{\text{Nascent.}}{2\,H.}$$
$$(2)\quad \underset{\text{Nascent.}}{3\,H} + HNO_3 = 2\,H_2O + NO.$$

On combining the two equations we get for the whole reaction—

$$3\,Cu + 8\,HNO_3 = 3\,Cu\,(NO_3)_2 + 2\,NO + 4\,H_2O.$$

The reaction may, however, be explained in another way, namely, by supposing that nitric acid first converts the metal into an oxide itself undergoing reduction, and then the oxide reacts with a further quantity of nitric acid, producing a nitrate of the metal and water—

$$(1).3\,Cu + 2\,HNO_3 = 3\,CuO + H_2O + 2\,NO.$$
$$(2)\quad CuO + 2\,HNO_3 = Cu(NO_3)_2 + H_2O.$$

It is beyond the scope of this book to discuss the relative merits of these two explanations.

The products of the reduction of nitric acid by metals may consist of any of the following substances: nitrogen peroxide, nitrous acid, nitric oxide, nitrous oxide, nitrogen and ammonia.

The exact course of the reaction depends upon the following factors:—

(1) The nature of the metal.
(2) The strength of the acid.
(3) The temperature.
(4) The concentration of the products in solution.

Thus we have seen that with moderately dilute acid copper forms chiefly nitric oxide; with strong nitric acid, however, the main product is nitrogen peroxide—

$$Cu + 4\,HNO_3 = Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2.$$

Again, zinc with dilute nitric acid yields chiefly nitrous oxide, but with a somewhat stronger acid a large proportion of ammonia results—

$$(1)\quad 4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O.$$
$$(2)\quad 4\,Zn + 9\,HNO_3 = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_3$$

The ammonia produced combines with the excess of nitric acid to produce ammonium nitrate—

$$NH_3 + HNO_3 = NH_4NO_3.$$

So that equation (2) is more correctly expressed—

$$4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + 3\ H_2O + NH_4NO_3.$$

The relative amount of reduction which nitric acid has undergone when the products nitrogen peroxide, nitrous acid, etc., are formed, can be well illustrated in the following manner, regarding nascent hydrogen as the reducing agent:—

$$\begin{aligned}
2\ HNO_3 + 2\ H &= 2\ H_2O + 2\ NO_2. \\
2\ HNO_3 + 4\ H &= 2\ H_2O + 2\ HNO_2. \\
2\ HNO_3 + 6\ H &= 4\ H_2O + 2\ NO. \\
2\ HNO_3 + 8\ H &= 5\ H_2O + N_2O. \\
2\ HNO_3 + 10\ H &= 6\ H_2O + N_2. \\
2\ HNO_3 + 16\ H &= 6\ H_2O + 2\ NH_3.
\end{aligned}$$

It will be noticed that the number of atoms of hydrogen required to reduce two molecules of nitric acid successively increases from nitrogen peroxide to ammonia.

The metals which *do* liberate free hydrogen from nitric acid are *magnesium* and *manganese*, the main products with the dilute acid being in both cases ammonia and hydrogen. When a metal such as mercury is capable of forming two nitrates the lower one is produced when the metal is in excess, the higher when the acid is in excess. Tin with quite dilute acid gives stannous nitrate, but with stronger acid it behaves in an unusual manner, being converted into stannic oxide, SnO_2—

$$Sn + 4\ HNO_3 = SnO_2 + 4\ NO_2 + 2\ H_2O.$$

Antimony is similarly oxidised to antimony pentoxide, Sb_2O_5.

191. **The passive state.**—Pure concentrated nitric acid does not attack iron, nickel or tin.

It was formerly supposed that the acid covered them with a coating of a higher oxide of the metal, which prevented the further action of the acid, rendering the metals "passive." Recently it has been suggested that the cause of the phenomenon is an electrical one, but the true explanation is still a matter of doubt.

192. **Aqua Regia.**—The so-called "noble" metals, such as gold and platinum, are not acted upon by nitric acid of any strength, but readily dissolve in a mixture of hydrochloric and nitric acids * which has for this reason been termed *aqua regia.*

The cause of the difference is that hydrochloric and nitric acids mutually interact setting free chlorine, which, especially in the nascent state, readily attacks gold and platinum—

$$3\ HCl + HNO_3 = NOCl + Cl_2 + 2\ H_2O.$$

193. **The Nitrates.**—These salts may be looked upon as nitric acid in which the hydrogen of the acid is replaced by a metal, thus—

$$\begin{array}{lllll} HNO_3 & KNO_3 & NaNO_3 & NH_4NO_3 & AgNO_3. \\ \left.\begin{array}{l} HNO_3 \\ HNO_3 \end{array}\right\} & Pb(NO_3)_2 & Cu(NO_3)_2 & Ca(NO_3)_2 & Ba(NO_3)_2. \end{array}$$

They may be produced by the action of the acid on the metals or on their oxides, hydroxides, or carbonates.

Exp. 133.—To a few cubic centimetres of *dilute* nitric acid contained in a porcelain basin add fragments of lead, and digest on a water-bath until the acid is saturated and no more of the metal will dissolve. Evaporate the clear liquid to dryness, when a white salt, nitrate of lead, remains.

Exp. 134.—Dilute 5 c.c. of nitric acid with an equal bulk of water, and add a little litmus solution, which will become of a bright red colour. Now add ammonia solution little by little until the last drop turns the litmus blue, and concentrate the liquid to a point at which, when a drop of it is allowed to cool on the end of a glass rod, it crystallises. On standing, crystals of ammonium nitrate will be obtained.

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* *Aqua regia* is usually made by mixing nitric acid with four times its volume of hydrochloric acid.

All the nitrates are soluble in water: those of the alkali metals are the most stable, and those of the heavy metals the least stable. When strongly heated all undergo decomposition.

Nitrates of the heavy metals evolve oxides of nitrogen (generally NO_2) and oxygen, leaving an oxide of the metal—

$$2\ Pb(NO_3)_2 = 2\ PbO + 4\ NO_2 + O_2.$$

Nitrates of the alkali metals (K, Na) evolve oxygen, leaving a nitrite—

$$2\ KNO_3 = 2\ KNO_2 + O_2.$$

Ammonium nitrate decomposes in an exceptional way, forming nitrous oxide and water—

$$NH_4NO_3 = N_2O + 2\ H_2O.$$

Nitrates when heated naturally exert a powerful oxidising action on substances which may be mixed with them.

Exp. 135.—Heat a few grammes of potassium nitrate in a test-tube until it fuses, and then drop into it one or two fragments of dry charcoal. The charcoal will ignite and burn with violence, being oxidised by the nitrate to CO_2.

Exp. 136.—Repeat the experiment, introducing a few small shavings of lead; the lead will be oxidised at the expense of the nitrate and transformed into a yellowish powder, oxide of lead.

194. Tests for Nitrates.—(1) Nitrates when heated with sulphuric acid or silica give off nitric acid fumes, often accompanied by red fumes of nitrogen peroxide.

(2) Mix a solution of a nitrate with strong sulphuric acid, and add copper turnings; on warming red fumes will be given off.

(3) (The most sensitive test). Mix a cold solution of a nitrate with a cold strong solution of ferrous sulphate, and pour gently down the side of the tube strong sulphuric acid: the latter sinks to the bottom, and a dark ring forms

above it. The sulphuric acid liberates nitric acid from the nitrate, and the ferrous sulphate reduces the nitric acid to nitric oxide, which combines with more ferrous sulphate to form the dark-coloured solution.

195. **Uses of Nitric Acid.**—Nitric acid is largely used in the manufacture of a number of important substances such as sulphuric acid, nitroglycerine, guncotton, colours, and nitrates. Among the last may be mentioned silver nitrate, which is used in photography, strontium and barium nitrates, which are used in pyrotechny, and lead nitrate which is employed in calico-printing. Nitric acid is also used in Grove's and Bunsen's electric batteries.

NITROUS ACID, HNO_2.

196. This acid is only known in dilute aqueous solution. It may be prepared by adding a strong acid such as hydrochloric acid to a solution of a nitrite, *e.g.* potassium nitrite, KNO_2—

$$KNO_2 + HCl = KCl + HNO_2.$$

The aqueous solution gradually decomposes at ordinary temperature, and more rapidly on warming, according to the equation—

$$3\ HNO_2 = HNO_3 + 2\ NO + H_2O.$$

Nitrous acid is capable of acting both as a reducing agent and as an oxidising agent; as the former towards substances which readily give up oxygen, and as the latter towards those which readily take up oxygen. Thus it is rapidly converted into nitric acid by potassium permanganate, the latter being reduced and decolorised. In the presence of dilute sulphuric acid the reaction which takes place may be thus represented—

$$5\ HNO_2 + 2\ KMnO_4 + 4\ H_2SO_4 = 2\ KHSO_4 + 2\ MnSO_4 + 5\ HNO_3 + 3\ H_2O.$$

On the other hand, nitrous acid liberates free iodine from potassium iodide. We may suppose that free hydriodic acid is first formed by double decomposition, and that this is then oxidised by the excess of nitrous acid—

$$KI + HNO_2 = KNO_2 + HI.$$
$$2\,HI + 2\,HNO_2 = 2\,H_2O + 2\,NO + I_2.$$

197. **Nitrites.**—The nitrites of the alkali metals may be formed—

(1) By heating the corresponding nitrates, *e. g.*—

$$2\,NaNO_3 = 2\,NaNO_2 + O_2.$$

If the nitrate is heated with certain metals, such as lead, the decomposition is brought about more readily, the metal taking up the oxygen—

$$\underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Lead.}}{Pb} = \underset{\text{Sodium nitrite.}}{NaNO_2} + \underset{\text{Lead oxide.}}{PbO.}$$

(2) By the action of nitrogen peroxide on the caustic alkalies. In this case nitrates are formed simultaneously—

$$2\,NO_2 + 2\,KOH = \underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + \underset{\substack{\text{Potassium}\\\text{nitrite.}}}{KNO_2} + H_2O.$$

All nitrites are soluble in water, but silver nitrite, $AgNO_2$, is only sparingly soluble, and is formed as a white precipitate when a strong solution of silver nitrate is mixed with a strong solution of sodium nitrite.

198. **Tests for Nitrites.**—(1) The evolution of red fumes (nitrogen peroxide) when the salt is treated with sulphuric acid.

(2) The formation of a dark ring at the surface of contact when a solution of ferrous sulphate is poured upon a solution of a nitrite, to which *dilute* sulphuric acid has been added (in some cases the addition of acid is unnecessary).

(3) The liberation of iodine from potassium iodide on the addition of an acid, *e. g.* sulphuric acid, and the decolorisation of potassium permanganate solution in presence of acetic acid.

NITROGEN PENTOXIDE, N_2O_5.

199. This is a white crystalline solid obtained by the action of a powerful dehydrating agent, such as phosphorus pentoxide, on nitric acid. The acid is introduced into a retort and well cooled by means of a freezing mixture. A quantity of phosphorus pentoxide equivalent to the acid used is gradually added, and on now gently warming the mixture nitrogen pentoxide distils over and is collected in a cooled receiver—

$$2\ HNO_3 + P_2O_5 = 2\ HPO_3 + N_2O_5.$$

A second method of preparation is to pass dry chlorine over dry silver nitrate—

$$4\ AgNO_3 + 2\ Cl_2 = 2\ N_2O_5 + 4\ AgCl + O_2.$$

Nitrogen pentoxide enters into combination with water with great energy, reproducing nitric acid; it is therefore the anhydride of this acid. It is an unstable body and undergoes decomposition with explosive violence when heated.

NITROGEN TETROXIDE OR PEROXIDE, N_2O_4 or NO_2.

200. **Preparation.**—Nitrogen peroxide is formed on the direct combination of nitric oxide, NO, with oxygen—

$$2\ NO + O_2 = N_2O_4.$$

It may also be prepared by heating lead nitrate—

$$2\ Pb(NO_3)_2 = 2\ PbO + 2\ N_2O_4 + O_2.$$

Exp. 137.—Introduce 10 grammes of finely-powdered lead nitrate into a retort of "hard" glass (see Fig. 52) connected with a U-tube surrounded by a freezing mixture (pounded ice or snow and salt) and heat strongly. Red fumes are given off and condense in the U-tube to a colourless liquid, N_2O_4. Remove the freezing mixture and note that as the temperature rises the liquid darkens in colour, and at ordinary temperatures is *orange yellow.*

Nitrogen peroxide is also formed to some extent when electric sparks are passed through a mixture of nitrogen and oxygen—

$$N_2 + 2\,O_2 = 2\,NO_2.$$

201. **Properties.**—The liquid obtained as in the experiment just described passes, on strongly cooling, into a colourless solid, melting at −10° C. If, on the other hand, its temperature is further raised it continues to get darker, and at 22° C. boils, giving off a reddish-brown vapour; the vapour, in its turn, continues to darken with rise of temperature till it becomes almost black. This change in colour is accompanied by a corresponding change in composition. Thus at low temperatures (−10° C.) nitrogen peroxide has the composition N_2O_4, and at 140° it has completely dissociated into NO_2 molecules, whilst at intermediate temperatures some of the molecules are N_2O_4, others are NO_2. That this is the true explanation is proved by the changes in density which the gas undergoes with rise of temperature.

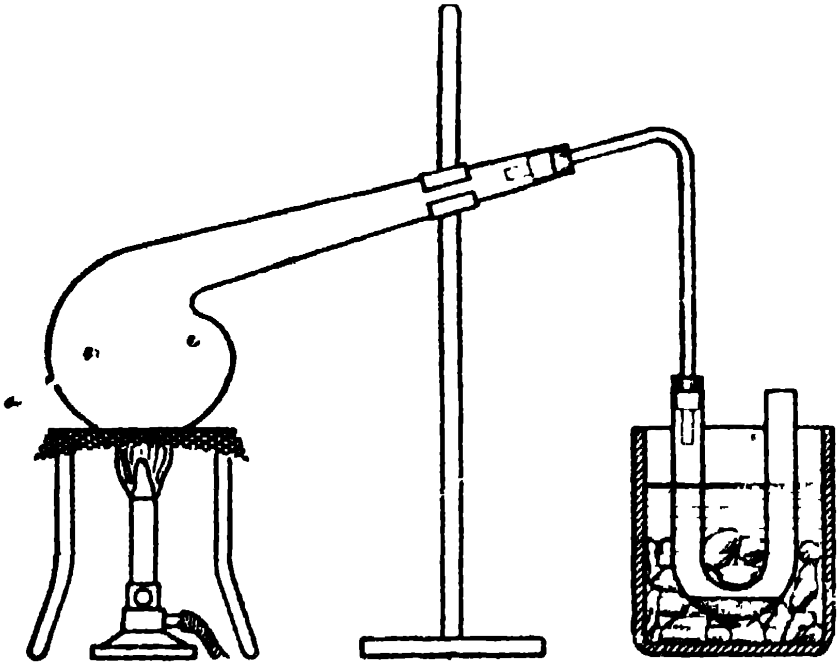

FIG. 52.

In the following table the values of the relative density ($H = 1$) are given for several different temperatures, and also the corresponding molecular weights.

Temperature.	Relative density.	Molecular weight.
26·7°	38·3	76·6
60·2°	30·1	60·2
100·1°	24·3	48·6
135·0°	23·1	46·2
140·0°	23·0	46·0

Now the molecular weight of N_2O_4 is 92, and that of NO_2 is 46, from which it follows that at 140° C. the dissociation into NO_2 molecules is complete, but at 26·7° C. the greater part of the gas consists of N_2O_4 molecules. By means of the lowering of freezing-point method of determining molecular weights, it has further been shown that at low temperatures nitrogen peroxide is composed of N_2O_4 molecules.

Nitrogen peroxide is not a supporter of combustion in the ordinary sense, *i. e.* it extinguishes a lighted taper, but substances which burn in oxygen and give out sufficient heat to decompose the nitrogen peroxide will also burn in the latter. Thus brightly burning phosphorus continues to burn in the gas with a dazzling light. Nitrogen peroxide is decomposed by water, the exact course of the reaction depending on the conditions. Thus with a small quantity of cold water, nitric and nitrous acids are produced—

$$H_2O + 2\,NO_2 = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Nitrous acid}}{HNO_2},$$

but with hot water the reaction proceeds thus—

$$H_2O + 3\,NO_2 = 2\,HNO_3 + NO.$$

This is what we might expect when we remember the ease with which nitrous acid decomposes into nitric acid and nitric oxide. During the solution of nitrogen peroxide in water the liquid passes through a series of colour changes—blue, green and orange. This is supposed to be due to the gradual solution of the nitrogen peroxide in the nitric acid formed. Of course, in the presence of sufficient water all the nitrogen peroxide is decomposed and the solution becomes colourless.

The gas attacks many metals, such as mercury, copper and iron. It is very poisonous.

NITROGEN TRIOXIDE, N_2O_3.

202. This oxide is obtained as a deep-blue liquid by passing nitric oxide into nitrogen peroxide, the temperature not being allowed to rise above − 21° C.

$$NO + NO_2 = N_2O_3.$$

Nitrogen trioxide is very unstable, and even at − 20° C. commences to decompose into nitrogen peroxide and nitric oxide—

$$N_2O_3 = NO + NO_2.$$

It cannot exist in the gaseous state.

We saw in § 196 that nitrous acid is produced by the action of a strong acid on a nitrite. At the same time, however, brown fumes are evolved, consisting of a gas which corresponds in percentage composition to nitrogen trioxide (*i. e.* the anhydride of nitrous acid) but really consists of a mixture of nitric oxide and nitrogen peroxide—

$$2\,KNO_2 + H_2SO_4 = K_2SO_4 + \underbrace{NO + NO_2}_{N_2O_3} + H_2O.$$

The same mixture of oxides is obtained by the action of nitric acid on arsenious oxide, As_2O_3—

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = \underset{\text{Arsenic acid.}}{2\,H_3AsO_4} + \underbrace{NO + NO_2}_{N_2O_3}.$$

If the brown fumes obtained by either of these processes are cooled down to − 21° C. combination takes place with formation of nitrogen trioxide.

NITRIC OXIDE, NO.

203. Preparation.—Nitric oxide is usually prepared by the action of moderately dilute nitric acid on copper. The reaction, which we have already discussed under Nitric Acid, is—

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Exp. 138.—Introduce a few grammes of copper turnings into an 8-ounce flask provided with a thistle funnel and delivery tube, and add about 50 c.c. of a mixture of equal parts of nitric acid and water. In a few moments gas begins to be evolved without the application of heat, and red fumes appear in the flask.

These red fumes are formed by the action of the nitric oxide on the oxygen contained in the flask; after a time the colour disappears as they are displaced, and the gas may then be collected over water at the pneumatic trough.

The gas so produced is not pure; it may contain other reduction products of nitric acid, such as nitrous oxide. The best method of preparing pure nitric oxide is to warm a solution of ferrous sulphate and potassium nitrate, acidified with dilute sulphuric acid—

$$6\,FeSO_4 + 5\,H_2SO_4 + 2\,KNO_3 = 3\,Fe_2(SO_4)_3 + 2\,KHSO_4 + 4\,H_2O + 2\,NO.$$

204. **Properties.**—Nitric oxide is a colourless gas not very soluble in water, which dissolves about $\frac{1}{20}$th of its volume of the gas under ordinary conditions. It is very difficult to liquefy, requiring a pressure of 104 atmospheres at − 11° C.; the liquid boils under normal pressure at − 93° C.

Nitric oxide by mere admixture with oxygen combines with it, as we have seen, giving rise to red fumes of nitrogen peroxide—

$$2\,NO + O_2 = 2\,NO_2.$$

Exp. 139.—Expose a jar of the gas to air, and observe the red fumes.

Exp. 140.—Pass oxygen little by little into a jar of the gas standing over water, allowing an interval to elapse between each addition. Red fumes will be formed, and these will dissolve in the water, which gradually rises in the jar. If the gas is pure and the oxygen be added in the proper proportion, the water will rise so as to completely fill the jar. A dilute solution of nitrous acid is thus formed, and may be shown to liberate iodine from potassium iodide, or to decolorise permanganate of potash.

Nitric oxide is the most stable of the oxides of nitrogen, and is only decomposed at a red heat (600° C.). It does not support combustion except when sufficient heat is evolved to decompose it, the oxygen which is liberated being the actual supporter of the combustion. Thus a lighted taper, burning sulphur and feebly burning phosphorus are extinguished by it, but fully ignited phosphorus continues to burn brightly.

Exp. 141.—Try whether a lighted taper, burning sulphur and phosphorus when just lighted, will continue to burn in the gas; then try phosphorus which has become fully ignited.

Nitric oxide dissolves readily in a solution of ferrous sulphate, forming a brown compound $(FeSO_4)_2 \cdot NO$. This is the compound forming the "brown ring" in the test for nitrates. On gently warming, this compound dissociates into ferrous sulphate and nitric oxide which is evolved in a pure state.

205. **Composition of Nitric Oxide.**—When iron is heated in nitric oxide it combines with the oxygen and sets free the nitrogen. The gas first expands by the heat, and the iron then burns forming triferric tetroxide, Fe_3O_4. On the completion of the reaction only nitrogen remains, and this gas will be found to occupy half the volume of the original gas. Hence one molecule of nitric oxide contains one atom of nitrogen, and its formula may be expressed N_1O_x. To determine the value of x we must ascertain the density of nitric oxide compared with hydrogen. It will be found to be 15, and since the hydrogen molecule, H_2, weighs 2, the molecule of nitric oxide must weigh $15 \times 2 = 30$, i. e.

$N_1O_x = 30$. But $N_1 = 14$; therefore $O_x = 30 - 14 = 16$. Now the atomic weight of oxygen is 16, and therefore $x = 1$, *i. e.* the molecule of nitric oxide is represented by NO.

NITROUS OXIDE, N_2O.

206. This gas is familiarly known as "laughing gas," because when breathed in small quantity it produces a feeling of exhilaration. Inhaled in larger quantities it is an anæsthetic, and renders the subject insensible to pain. It is for this reason employed in dentistry.

Preparation.—It has already been pointed out (§ 190) that when nitric acid (dilute) is acted upon by zinc, nitrous oxide is formed. It is more usual, however, to prepare it by heating ammonium nitrate, the decomposition being represented by the equation—

$$NH_4NO_3 = N_2O + 2\ H_2O.$$

Exp. 142.—Introduce about 30 grammes of dry ammonium nitrate into a 4-ounce flask and heat gently—just so as to bring about a steady and not too rapid evolution of the gas. The delivery tube should be wider than usual, as the salt is liable to be carried over and to stop up the tube; also stop the experiment when about two-thirds of the salt has been decomposed or an explosion may ensue. Cold water dissolves about its own volume of the gas; it may, however, be collected over hot water.

207. **Properties of Nitrous Oxide.**—It is a colourless gas with an agreeable odour and taste. It condenses at 15° C. under a pressure of 40 atmospheres to a liquid which boils at $-92°$ C. under ordinary pressure. One hundred volumes of water dissolve 130 volumes of the gas at 0° C., 92 at 10° C., and 67 at 20° C.

It is easily decomposed by heat, and supports combustion almost as readily as oxygen.

Exp. 143.—Plunge a glowing taper into a jar of nitrous oxide, and it will burst into flame just as it does in oxygen. Sulphur and phosphorus also burn in the gas with almost as much vigour as in oxygen, though if only feebly ignited they may be extinguished. To distinguish it from oxygen, pass nitric oxide into the gas; no red fumes will appear.

208. Composition of Nitrous Oxide.—The composition of the gas may be determined by the combustion of potassium in it and by an estimation of the density. The combustion experiment may be carried out in the apparatus shown in Fig. 53, the gas being confined over mercury. It will be found that when the residual gas has cooled down to the ordinary temperature there is no change in volume, showing that nitrous oxide contains its own volume of nitrogen. The formula must therefore be N_2O_x. But the density is 22, corresponding to a molecular weight 44; therefore the weight of oxygen in a molecule of nitrous oxide is $44 - 2 \times 14 = 16$. It follows that $x = 1$, and the formula is N_2O.

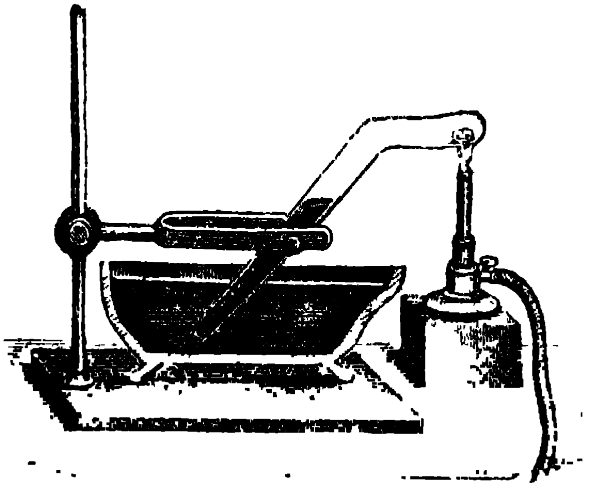

FIG. 53.

The composition may also be determined by exploding with excess of hydrogen in a eudiometer, when the reaction is—

$$N_2O + H_2 = H_2O + N_2.$$

The residual gas consists of nitrogen and excess of hydrogen; the amount of the latter is estimated by exploding with excess of oxygen when two-thirds of the diminution in volume represents the hydrogen present.

QUESTIONS.—CHAPTER XVII.

1. How do you account for the occurrence of oxides of nitrogen, and the oxyacids or salts of these, in the air and in the soil?
2. What is the effect of distilling (*a*) very dilute nitric acid, (*b*) pure nitric acid?
3. Describe an experiment by which oxygen gas can be obtained from nitric acid.
4. Give striking experiments calculated to illustrate in regard to nitric acid, (*a*) its powerful oxidising action; (*b*) its powerful solvent action.
5. What explanations have been given of the action of dilute nitric acid on copper?
6. Compare the action of nitric acid of different strengths on the metals, zinc, copper and tin. Give equations.
7. Explain what is meant by the *passive state*.
8. What is *aqua regia*, and on what does its special power as a solvent of metals depend?
9. How would you prepare the nitrates of lead and potassium, and obtain them in the form of crystals?
10. Give an account of the action of heat on metallic nitrates.
11. Describe three tests which are characteristic of nitrates.
12. What are the chief uses of nitric acid?
13. What is the action of heat on a solution of nitrous acid?
14. Give examples (with equations) of (*a*) the oxidising action, (*b*) the reducing action of nitrous acid.
15. By what chemical reactions may nitrites be distinguished from nitrates?
16. What is the action of chlorine on dry silver nitrate?
17. How is nitric anhydride usually prepared, and what are its chief properties?
18. How is the tetroxide of nitrogen obtained? Discuss the action of heat on this substance.
19. Under what conditions does nitrogen peroxide become a supporter of combustion?

20. What is the action of water on nitrogen peroxide?
21. Under what conditions does nitrogen trioxide exist, and how is it prepared?
22. How may *pure* nitric oxide be obtained?
23. What are the properties of nitric oxide, and how may it be distinguished from nitrous oxide?
24. Demonstrate that the chemical formula of nitric oxide is NO.
25. Give two methods for the preparation of nitrous oxide.
26. State the *physical* properties of nitrous oxide, and say how you would distinguish by chemical tests nitrous oxide from oxygen. In what respects does it resemble oxygen?

CHAPTER XVIII.

SULPHUR. SULPHURETTED HYDROGEN.

SULPHUR.

209. **Occurrence.**—Sulphur is one of the comparatively few elements which occur in quantity in the uncombined condition. In Europe it is found in the neighbourhood of active or extinct volcanoes in Italy, Sicily, Iceland, etc., being usually associated with mineral matter. In combination with hydrogen it is found as sulphuretted hydrogen in certain mineral springs, and with metals as mineral sulphides, such as iron pyrites, FeS_2; galena, PbS; zinc blende, ZnS; and cinnabar, HgS. Sulphates of lime (gypsum) and barium (heavy spar) also occur in some localities in considerable quantity. We see then that sulphur either free or in combination is widely distributed.

210. **Extraction.**—Sulphur melts at 115° C., and in the molten condition can be run off from the earthy impurities and obtained in a state of moderate purity. The process is carried out as follows :—Impure native sulphur is stacked in a brick kiln on a sloping floor, vertical air spaces being left at intervals. The sulphur is lighted at the bottom ; a small quantity burns and the heat produced melts out the rest. The melted sulphur runs down the sloping floor and collects in a trough placed to receive it.

Sulphur boils at 440° C., giving off brownish-red vapours which readily condense again on cooling, and the further purification of the sulphur may be effected by distillation in an iron retort, the vapours being passed into a brick chamber where they condense. (Fig. 54.) At the outset when the chamber is cool the product obtained is a fine powder, called "flowers of sulphur," for just as water vapour at temperatures below zero (the melting-point of ice) condenses in the form of snow, so in the case of sulphur there is formed by rapid cooling finely-divided sulphur.

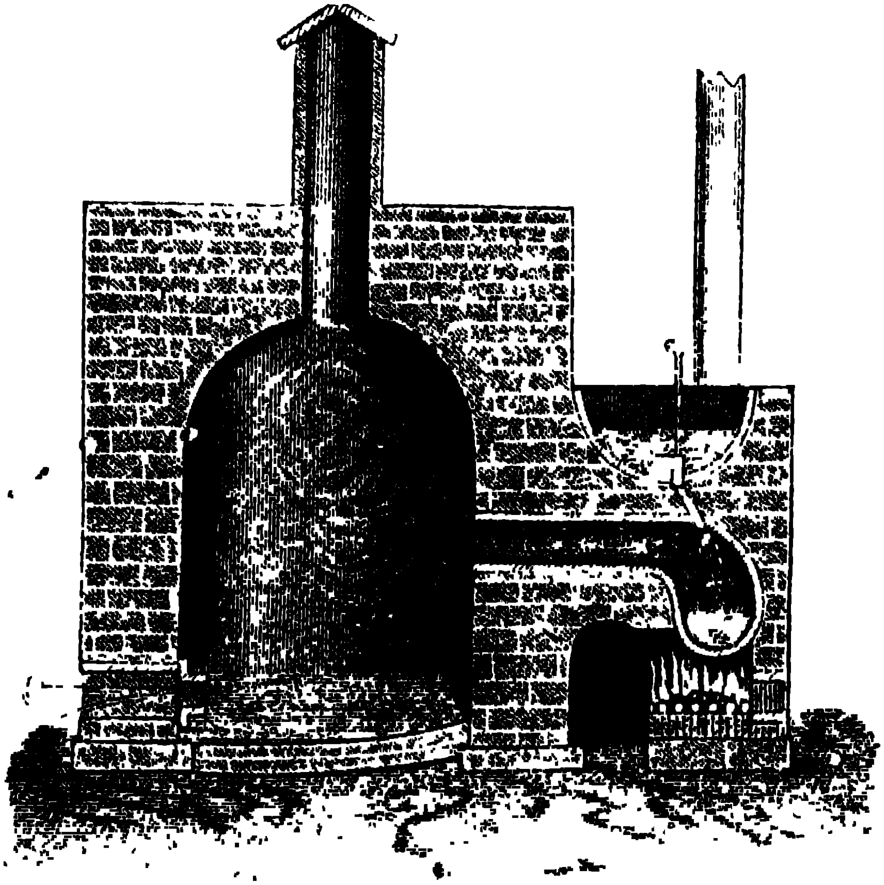

FIG. 54.

When the temperature of the chamber rises above the melting-point of sulphur (115° C.), the product of the condensation is *liquid* sulphur, and this is run off into moulds where it is cast into sticks known familiarly as "brimstone."

211. Physical changes of Sulphur under the action of Heat.

Exp. 144.—Put about 30 grammes of sulphur in a wide test-tube, and heat it as evenly as possible in the flame of a Bunsen burner. At 115° C. it will be seen to melt, and at a slightly higher temperature it forms a limpid liquid of a pale yellow colour. As it gets hotter the liquid grows more viscid and darker in colour, till at 250° C. it becomes almost solid and nearly black. Above 250° C. it again becomes more mobile, and at 440° C. it boils and gives off a brownish-red vapour. Pour some of the sulphur at about 350° C. in a thin stream into a beaker of water, and note the production of plastic sulphur.

212. **Allotropic modifications of Sulphur.**—Sulphur exists in several forms which show marked differences in their physical properties. These may be classified as follows:—

- (*a*) Crystalline forms:
  - (1) Octahedral sulphur.
  - (2) Prismatic sulphur.
- (*b*) Amorphous forms:
  - (1) Plastic sulphur.
  - (2) White amorphous sulphur.
  - (3) Yellow amorphous sulphur.
- (*c*) Colloidal sulphur.

Octahedral Sulphur.—Sulphur is found naturally in rhombic octahedra (see Fig. 55), and it is in this form that it separates out from solvents, such as bisulphide of carbon, on slow evaporation. The specific gravity of rhombic sulphur is 2·045.

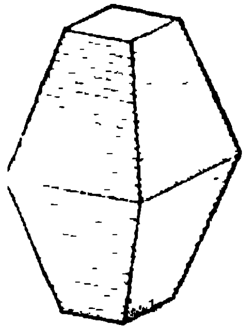
Fig. 55.

Prismatic Sulphur.—Sulphur in this form is no longer rhombic, but monoclinic; it is also of lower specific gravity, 1·93, and melts at 120° instead of 115°, and when left at the ordinary temperature for some time, breaks up and passes into the more stable rhombic form, as, indeed, all the modifications tend to do. It is soluble in carbon bisulphide.

Exp. 145.—Melt about 500 grammes of sulphur in a clay crucible, and allow it to cool until a crust forms at the surface; the crust is then pierced and the still liquid portion poured out. Beneath the crust and on the sides of the crucible will be found long prismatic needles of sulphur.

Plastic Sulphur.—As already stated, this form of sulphur is obtained by pouring sulphur at a temperature of 350° C. into cold water. Whilst in the crystalline form sulphur is brittle; in this condition, as the name implies, it can be moulded with the fingers, or drawn out into long flexible threads. Unlike the modifications previously described, it is insoluble in carbon disulphide: its specific gravity is 1·95. On standing, it slowly hardens and passes into the ordinary form of sulphur.

White Amorphous Sulphur.—When hydrochloric acid is added to a solution of a polysulphide, *e. g.* calcium polysulphide or yellow ammonium sulphide, a white very finely-divided precipitate of amorphous sulphur is produced, called "milk of sulphur." This precipitate is insoluble in carbon bisulphide. If sodium thiosulphate ($Na_2S_2O_3$) is used instead of a polysulphide, a similar white precipitate of sulphur is at first produced, but this gradually turns yellow, when it becomes soluble in carbon bisulphide (being converted into the crystalline rhombic variety)—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + S + SO_2 + H_2O.$$

Exp. 146.—Make a moderately concentrated solution of sodium thiosulphate, or of an alkaline polysulphide (*e. g.* solution of yellow ammonium sulphide), and add a few drops of hydrochloric acid. The solution becomes turbid, and a white precipitate of "milk of sulphur" is produced.

Note that in the case of the thiosulphate the precipitate gradually turns yellow. Now add some carbon bisulphide and shake up; the yellow crystalline precipitate dissolves, leaving a white precipitate of unchanged amorphous sulphur.

This variety of sulphur has a specific gravity 1·82.

Yellow Amorphous Sulphur.—"Flowers of sulphur" obtained as already described consists chiefly of small crystals of octahedral sulphur, but also contains a small percentage of an amorphous modification. The latter is insoluble in carbon bisulphide, and can therefore be obtained by treating flowers of sulphur with this liquid, when the octahedral sulphur dissolves, and the amorphous portion remains behind as a light yellow powder of specific gravity 1·96. This form is also produced when sulphur dichloride (S_2Cl_2) is decomposed by water—

$$2\ S_2Cl_2 + 3\ H_2O = 4\ HCl + 3\ S + H_2O + SO_2.$$

Colloidal Sulphur is soluble in water and is obtained when solutions of sulphuretted hydrogen and sulphur dioxide are mixed—

$$SO_2 + 2\ H_2S = 2\ H_2O + 3\ S.$$

213. **Proof that the Allotropic Modifications of Sulphur consist of the same Element.**—On burning a known weight of any form of sulphur in oxygen and weighing the sulphur dioxide produced, it is found that in all cases the ratio of the weight of sulphur dioxide formed to that of sulphur burnt is 64 : 32, which agrees with the equation—

$$\underset{32}{S} + \underset{2 \times 16}{O_2} = \underset{32 + 2 \times 16 = 64}{SO_2}.$$

This proves that each of the different forms consists wholly of the same element. The experiment may be carried out as follows:—A small fragment of sulphur (about 0·2 gramme) is weighed out accurately in a porcelain "boat" (A, Fig. 56). This is introduced into a piece of hard glass tubing in the position shown in the diagram. A series of bulbs, B, containing strong caustic potash solution, are weighed together with a small calcium chloride tube C, and then attached to the end of the tube remote from the porcelain boat. The other end of the tube is connected with a supply of dry oxygen. The boat is now gently heated by means of a Bunsen burner, and a slow current of oxygen is passed through the tube. The sulphur burns forming sulphur dioxide, which is absorbed in the potash bulbs. Any moisture driven out of the bulbs by the current of gas is absorbed by the calcium chloride in C, which, it will be remembered, was weighed along with the bulbs; thus an error in the final weight of the bulbs due to loss of water vapour is avoided. When all the sulphur has disappeared, and no more absorption is observed to be taking place in the bulbs, they are disconnected and re-weighed (along with the calcium chloride tube), after allowing them to cool. The increase in weight gives the weight of sulphur dioxide. If any sulphur vaporises and condenses in the cooler part of the tube this must be gently heated by a Bunsen burner till it becomes oxidised.

214 **Combination of Sulphur with other elements.**—Sulphur combines with many elements when heated with them. Thus it burns in oxygen at about 400° C., and it combines with carbon at a red heat, forming carbon disulphide, CS_2, while chlorine and hydrogen passed into boiling sulphur give sulphur monochloride, S_2Cl_2, and sulphuretted hydrogen respectively.

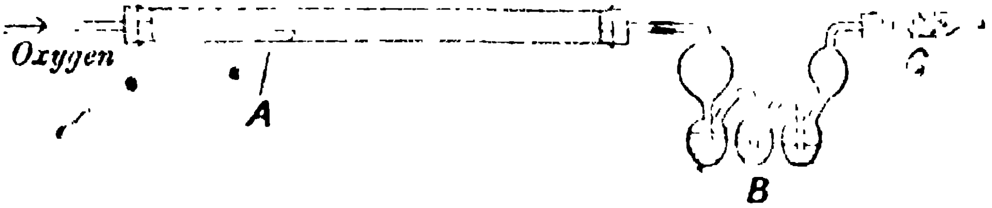

FIG. 56.

Many metals combine with sulphur when heated with it; for example, iron (see Exp. 64), silver, forming silver sulphide, Ag_2S, and copper, forming cuprous sulphide, Cu_2S.

Exp. 147.—Heat sulphur to the boiling-point and until the upper part of the tube is filled with its vapour, and then plunge into it thin sheet copper, or Dutch metal; the metal glows, and enters into combination with the sulphur to form sulphide of copper.

215. **Uses of Sulphur.**—Sulphur is largely used in the arts for the production of matches, gunpowder, sulphuric acid, and as a source of sulphurous acid for bleaching wool, straw and silk.

Sulphuretted Hydrogen, H_2S.

216. **Occurrence.**—Sulphuretted hydrogen occurs in solution in certain mineral waters (*e. g.* those at Harrogate), and is formed during the putrefaction of animal and vegetable matters which contain sulphur.

217. **Preparation.**—The gas is most conveniently prepared by the action of dilute sulphuric acid, or dilute hydrochloric acid on ferrous sulphide—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

The best form of apparatus to use when a continuous supply of the gas is required is that shown in Fig. 57. The upper bottle contains the dilute acid, and the lower one the ferrous sulphide in lumps about the size of a walnut. The two bottles are connected by rubber tubing, on which is placed a clip, A. The mouth of the lower bottle is fitted with a cork, through which passes a delivery tube provided with a stopcock, B, which is kept closed except when a supply of the gas is required. When this is the case the clip is loosened and a little acid allowed to run down on to the ferrous sulphide; the gas is led away by the delivery tube and passed through a wash-bottle containing a little water to remove impurities. To stop the supply of gas B is closed, and the ferrous sulphide bottle is raised so that

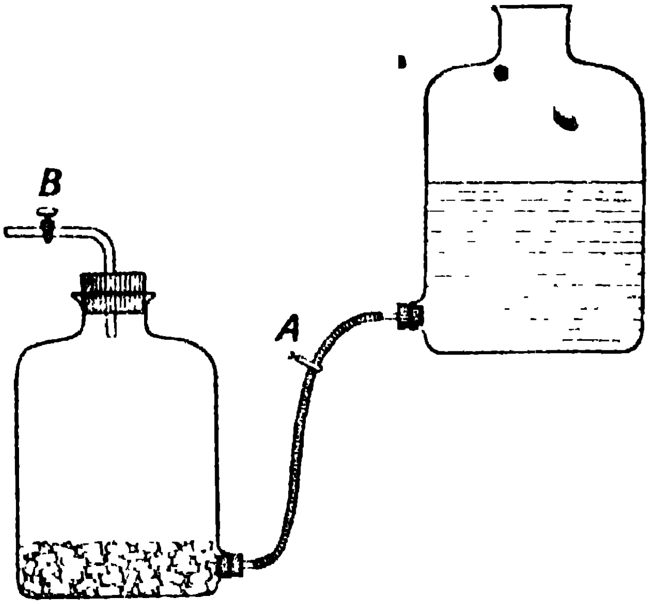

Fig. 57.

the acid in it flows back into the acid bottle. H_2S cannot be collected over cold water as it is too soluble; and owing to its offensive nature, and to the fact that it is only slightly heavier than air, it should not be collected by displacement of air; also mercury is inadmissible because it attacks the gas. Since, however, the solubility in water rapidly decreases with rise in temperature, *hot* water may be used.

If only a small quantity of sulphuretted hydrogen is required, a Wolff's bottle provided with a thistle funnel and delivery tube may replace the apparatus above described.

The gas obtained in this way always contains free hydrogen on account of the iron present in the ferrous sulphide (which is prepared by heating iron and sulphur together). To obtain *pure* sulphuretted hydrogen, sulphide of antimony is heated in a flask with *concentrated* hydrochloric acid—

$$Sb_2S_3 + 6\ HCl = \underset{\text{Antimony chloride.}}{2\ SbCl_3} + 3\ H_2S.$$

The gas is passed through a wash-bottle containing water to remove hydrochloric acid, and may then be collected as before. If *dry* sulphuretted hydrogen is required, the gas, after washing, should be passed through a U-tube containing calcium chloride to absorb the water vapour (sulphuric acid cannot be used because it reacts with the gas).

Sulphuretted hydrogen is also produced when hydrogen and sulphur vapour are passed together through a red-hot tube.

218. **Properties.**—Sulphuretted hydrogen is a colourless gas with a disagreeable odour, and is poisonous if inhaled in quantity. It is moderately soluble in water, which at 0° C. and 760 mm. pressure dissolves 4·37 times its volume of the gas, and at 20°, 2·9 times its volume. The aqueous solution possesses the characteristic smell of the gas, and has a faintly acid reaction. Sulphuretted hydrogen burns with a blue flame, forming water vapour and sulphur dioxide in a free supply of oxygen or air, whilst in a limited supply of air free sulphur is formed—

$$2\ H_2S + 3\ O_2 = 2\ H_2O + 2\ SO_2.$$
$$2\ H_2S + \ O_2 = 2\ H_2O + 2\ S.$$

Exp. 148.—Prepare sulphuretted hydrogen by the action of dilute sulphuric acid on ferrous sulphide; wash the gas by passing through a little water contained in a flask, and collect a cylinder over hot water. Apply a lighted taper to the mouth, and note that the gas burns with a pale blue flame, and that a gas (SO_2) is formed which has the suffocating odour of burning sulphur. There is usually a slight deposit of sulphur on the sides of the vessel due to the cooling of the gas, and the difficulty of access of air in sufficient quantity to ensure complete combustion.

If the taper be passed within the cylinder in which the gas is burning, it will be extinguished, showing that sulphuretted hydrogen, like hydrogen, burns in air (or oxygen), but does not support the combustion of a taper.

Whilst performing this experiment you will have noticed the obnoxious odour of the gas.

Exp. 149.—Fit the generating apparatus with a tube about 20 centimetres long, drawn out to a fine jet. The gas may be lighted at the jet when all the air is expelled, and the presence of water in the products of combustion may be shown by holding a cool glass vessel over the flame. Also, by depressing the lid of a porcelain crucible into the flame, a deposit of sulphur may be obtained. Now heat the tube some distance away from the orifice with a Bunsen burner or spirit-lamp, and the gas will be decomposed by the heat, and a deposit of sulphur will form a little beyond the point where the heat is applied. Finally, extinguish the flame, and allow the gas to impinge on a piece of filter-paper moistened with nitrate (or acetate) of lead; a dark stain will be produced owing to the formation of sulphide of lead: by this test the presence of sulphuretted hydrogen may be detected even when present in very small quantities.

We have seen in the experiment just performed that sulphuretted hydrogen is easily decomposed by heat. It is also very readily broken up by the action of metals, many of which act upon it even at ordinary temperature; the metal combines with the sulphur, and free hydrogen is liberated. The tarnishing of silver when exposed to the air of towns is an example of this; the air contains a small percentage of sulphuretted hydrogen produced during the combustion of coal, which usually contains a small quantity of iron pyrites (FeS_2); this H_2S in the air attacks the silver, producing a layer of silver sulphide, which is black. On heating many metals in the gas the same change is brought about much more rapidly; tin and cadmium, for instance, very readily bring about the complete decomposition of a confined volume of the gas on the application of gentle heat—

$$Sn + H_2S = SnS + H_2.$$

As might be expected from the ease with which the gas is decomposed with liberation of hydrogen, sulphuretted hydrogen belongs to the class of reducing agents. For example, it reduces sulphuric acid to sulphur dioxide, and ferric chloride to ferrous chloride, according to the equations—

$$\begin{aligned} H_2S + H_2SO_4 &= SO_2 + 2\,H_2O + S. \\ 2\,FeCl_3 + H_2S &= 2\,FeCl_2 + 2\,HCl + S. \end{aligned}$$

Again, potassium permanganate and potassium bichromate in the presence of dilute sulphuric acid are reduced to manganous sulphate and chromic sulphate respectively—

$$\begin{aligned} 2\,KMnO_4 + 5\,H_2S + 4\,H_2SO_4 &= 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,S. \\ K_2Cr_2O_7 + 3\,H_2S + 5\,H_2SO_4 &= 2\,KHSO_4 + Cr_2(SO_4)_3 + 7\,H_2O + 3\,S. \end{aligned}$$

In all these cases free sulphur is liberated. The action of the halogens on the gas has already been referred to in Chap. XIV.

219. Sulphides.—The formation of the sulphides of the metals can conveniently be studied by experiment.

Exp. 150.—Make a solution of sulphuretted hydrogen in water, and dip in it a blue litmus paper; it will be slightly reddened, showing that sulphuretted hydrogen is a weak acid. By replacing the hydrogen of the acid by metals sulphides are produced.

Pour a few c.c. of it into neutral solutions of copper sulphate, lead nitrate, nickel sulphate, zinc sulphate, calcium chloride, sodium chloride. The following results will be noticed:—

With copper sulphate, a black precipitate of cupric sulphide—

$$CuSO_4 + H_2S = \underset{\text{Cupric sulphide.}}{CuS} + H_2SO_4.$$

With lead nitrate, a black precipitate of lead sulphide—

$$Pb(NO_3)_2 + H_2S = \underset{\text{Lead sulphide.}}{PbS} + 2\,HNO_3.$$

With nickel sulphate, a black precipitate of nickel sulphide—

$$NiSO_4 + H_2S = \underset{\text{Nickel sulphide.}}{NiS} + H_2SO_4.$$

With zinc sulphate, a white precipitate of zinc sulphide—

$$\underset{}{ZnSO_4} + H_2S = \underset{\text{Zinc sulphide.}}{ZnS} + H_2SO_4.$$

The same effects are produced by passing H_2S *gas* into solutions of the above salts.

In the case of calcium chloride and sodium chloride there will be no precipitate, owing to the fact that the sulphides of calcium and sodium are readily soluble in water.

Now add some hydrochloric acid to the tubes containing the precipitates, and the sulphides of nickel and zinc will be found to dissolve, whilst those of copper and lead will remain.

By such a method we may prepare many of the sulphides of the metals, and we shall find them divisible into the following classes—

(1) Sulphides insoluble in water and dilute mineral acids.
(2) Sulphides which are insoluble in water, but soluble in dilute mineral acids.
(3) Sulphides which are soluble even in water.

The precipitate may be separated by filtration from the solution which remains, and it is possible in this way to separate any member or members of one of these classes from those of another class.

Many of the sulphides may also be prepared by mixing the metal (preferably in a finely-divided condition or in filings) intimately with excess of powdered sulphur and heating in a porcelain crucible until the portion of sulphur over and above that which will enter into combination with the metal is volatilised. Access of air or of gases which may act upon the sulphide is to be avoided.

When strong aqueous ammonia is saturated with sulphuretted hydrogen the product consists of a solution of ammonium sulphide $(NH_4)_2S$, ammonium hydrogen sulphide, $NH_4{\cdot}HS$, and ammonium hydroxide; this solution is known as "ammonium sulphide." On allowing it to stand in contact with the air it undergoes partial oxidation with formation of free sulphur, which then combines with more ammonium sulphide to form polysulphides of the general formula $(NH_4)_2S_x$, where x may be as high as 9. These polysulphides are yellow, and so the solution of ammonium sulphide which is colourless at first gradually turns yellow and is then known as "yellow ammonium sulphide." Yellow ammonium sulphide is largely employed as a reagent in qualitative analysis.

220. **Tests for Sulphides.**—(1) Warm the substance with dilute sulphuric acid; *most* sulphides are decomposed with the evolution of sulphuretted hydrogen, *e.g.*—

$$\underset{\text{Ferrous sulphide}}{FeS} + H_2SO_4 = \underset{\text{Ferrous sulphate.}}{FeSO_4} + H_2S.$$

The sulphuretted hydrogen may be detected by its odour or by its action on paper moistened with a solution of acetate of lead, $Pb(C_2H_3O_2)_2$.

(2) Mix a little of a dry sulphide with sodium carbonate and heat strongly on charcoal with the blowpipe flame. Sulphide of sodium is formed, and may be recognised by the fact that when a little of the product is placed on a silver coin and moistened, a brown stain is produced. All sulphides react in this way.

221. **Composition of Sulphuretted Hydrogen.**—When sulphuretted hydrogen is heated alone or with metallic tin it yields its own volume of hydrogen. (The gas and tin are heated in a glass tube closed by a cork. When the tube has cooled the cork is removed under water. No gas escapes and water does not rise in the tube.) By Avogadro's Law it follows that one molecule of sulphuretted hydrogen yields and contains one molecule, *i.e.* two atoms, of hydrogen. Call the number of atoms of sulphur in the gas x; then the formula may be written H_2S_x. The simplest way to find x is to determine the molecular weight of sulphuretted hydrogen from its density. It is found that the relative density of the gas is 17 ($H = 1$); the molecular weight is, therefore, $2 \times 17 = 34$, and so

Molecular weight of sulphuretted hydrogen	=	34
Weight of hydrogen in a molecule of sulphuretted hydrogen	=	2
,, ,, sulphur ,, ,, ,,	=	32

But 32 is the atomic weight of sulphur; hence the molecule of sulphuretted hydrogen contains one atom of sulphur, i.e. $x = 1$, and the formula becomes H_2S.

QUESTIONS.—CHAPTER XVIII.

1. How is sulphur separated from the mineral matter with which it is associated in the native condition?
2. Under what conditions are "flowers" of sulphur and "milk" of sulphur formed?
3. Describe the physical changes through which sulphur passes when it is heated in the absence of air.
4. Tabulate the properties of the different allotropic modifications of sulphur so as to bring out the differences between them.
5. Describe the preparation of (*a*) prismatic sulphur, (*b*) plastic sulphur.
6. What is the action of sulphur vapour on heated copper, iron, oxygen, hydrogen and chlorine respectively? Give equations representing the changes which occur.
7. How would you prove that octahedral and prismatic sulphur consist of the same element?
8. How would you prepare and collect a specimen of *pure dry* sulphuretted hydrogen?
9. What products are obtained by burning sulphuretted hydrogen (*a*) in a limited supply of air, (*b*) in excess of air?
10. Give examples with equations of the reducing action of sulphuretted hydrogen.
11. What is the action of sulphuretted hydrogen on acid solutions of (*a*) silver nitrate, (*b*) copper sulphate, (*c*) lead nitrate? Give equations showing the changes which take place.
12. How would you show (*a*) that sulphuretted hydrogen contains hydrogen and sulphur, (*b*) that it contains these elements in the proportions represented by the formula H_2S?
13. What is the composition of "yellow ammonium sulphide"?

CHAPTER XIX.

OXIDES AND OXYACIDS OF SULPHUR.

222. SULPHUR forms four compounds with oxygen, namely, sulphur dioxide, SO_2, sulphur trioxide, SO_3, sulphur sesquioxide, S_2O_3, and sulphur heptoxide, S_2O_7. Two of these oxides, SO_2 and SO_3, combine with water to produce corresponding acids, sulphurous acid, H_2SO_3, and sulphuric acid, H_2SO_4, and they are therefore the anhydrides of these acids. The other two oxides do not produce the corresponding acids on treatment with water, though these acids can be obtained by other methods. The full list of the oxyacids of sulphur is—

Sulphurous acid	H_2SO_3
Sulphuric acid	H_2SO_4
Nordhausen sulphuric acid	$H_2S_2O_7$
Thiosulphuric acid	$H_2S_2O_3$
Hyposulphurous acid	$H_2S_2O_4$
Persulphuric acid	$H_2S_2O_8$
Dithionic acid	$H_2S_2O_6$
Trithionic acid	$H_2S_3O_6$
Tetrathionic acid	$H_2S_4O_6$
Pentathionic acid	$H_2S_5O_6$
Hexathionic acid	$H_2S_6O_6$.

We shall only study the more important of these compounds, viz. sulphur dioxide, sulphur trioxide, sulphurous acid, sulphuric acid and thiosulphuric acid.

SULPHUR DIOXIDE, SO_2.

223. Preparation.—When sulphur burns in air or oxygen, sulphur dioxide is formed, and for purposes in which admixture with nitrogen or the excess of oxygen is of no moment, the gas may be prepared by this method. On the manufacturing scale indeed sulphur dioxide is sometimes so obtained, though more usually a sulphide containing a large proportion of sulphur, such as iron pyrites, FeS_2, is employed (see § 232).

When the gas is required in a tolerably pure condition the following method is applicable :—

Exp. 151.—About 20 grammes of metallic copper are placed in an eight-ounce flask provided with a thistle funnel and delivery tube, and 50 c.c. of concentrated sulphuric acid are poured down the funnel. The flask is then heated on a sand-bath, moderating the heat so soon as the action commences. The reaction which takes place is a complex one, but consists essentially in the reduction of the sulphuric acid by copper. The latter is converted chiefly into $CuSO_4$ and Cu_2S.

Mercury, charcoal, or sulphur may be substituted for copper, but in the case of charcoal the gas which passes off is mixed with carbon dioxide :—

$$C + 2\,H_2SO_4 = CO_2 + 2\,H_2O + 2\,SO_2.$$

With sulphur the reaction is—

$$S + 2\,H_2SO_4 = 2\,H_2O + 3\,SO_2,$$

sulphur dioxide being formed both from the sulphur itself and from the sulphuric acid used. It remains to be added that all sulphites when treated with a mineral acid yield sulphur dioxide—

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + 2\,H_2SO_4 = \underset{\text{Sodium hydrogen sulphate.}}{2\,NaHSO_4} + H_2O + SO_2.$$

Sulphur dioxide being very soluble in water cannot be collected over this liquid; mercury may however be used, but as the gas is more than twice as heavy as air it may be conveniently collected by displacement of air. Several jars may be filled with it, and its properties demonstrated by the experiments given below.

224. Properties.—Sulphur dioxide is a heavy colourless gas having a suffocating odour. At 760 mm. pressure water at zero dissolves 80 times its volume of the gas, and at 10° C. 56 times its volume, the solution having an acid reaction. Sulphur dioxide condenses to a liquid under ordinary atmospheric pressure at $-8°$ C., and under 2 atmospheres pressure at 0° C. It can therefore be obtained in the liquid form by passing the gas into a vessel surrounded by a freezing mixture of ice and salt.

Exp. 152.—Put a lighted taper into a jar of the gas; it will be extinguished, nor will the gas itself burn. Metallic potassium when previously ignited will however burn at the expense of the oxygen in this gas.

Exp. 153.—Show the great solubility of the gas by the method used in Experiment 118 (§ 149), or by passing the gas through 10 c.c. of water until a saturated solution is obtained. Note the acid properties of the solution, and that it possesses the odour of the gas.

225. **Reducing action of Sulphur Dioxide.**—Sulphur dioxide is a strong reducing agent; its powers as an antiseptic and as a medium for bleaching silk, straw and wool are due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter; sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—

$$Cl_2 + H_2O = 2\,HCl + \underset{\text{Nascent oxygen.}}{O},$$

the other liberates *hydrogen*—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nascent hydrogen.}}{2\,H}$$

The nascent hydrogen produced then combines with the colouring matter to produce a colourless compound. In many cases the colour is restored by exposure to air, when the oxygen of the air oxidises the colourless compound back to the original coloured substance. In some cases of bleaching by sulphur dioxide the coloured compound *combines directly with SO_2*; in such cases the colour may be restored by the addition of an acid which decomposes the colourless addition product with evolution of sulphur dioxide. The SO_2 addition product may also be acted upon by the oxygen and moisture of the air, whereby the SO_2 is converted into sulphuric acid and the coloured compound again set free.

Exp. 154.—Throw some rose-leaves into a solution of sulphur dioxide; they are bleached. Now add a few drops of strong sulphuric acid; the colour is restored. Bleach some more of the leaves in the same manner, remove them from the solution, and leave them exposed to the air for some time. The colour will gradually return.

It must be noted that an aqueous solution of sulphur dioxide does not undergo decomposition in the complete absence of air or other oxidising agent; water and sulphur dioxide do not react to give sulphuric acid and hydrogen unless there is some substance present to take up the hydrogen. In the presence of air the solution gradually absorbs oxygen, and the following change takes place—

$$2\,SO_2 + 2\,H_2O + \underset{\text{From the air.}}{O_2} = 2\,H_2SO_4.$$

Another good example of the reducing action of sulphur dioxide is its power of converting ferric salts into ferrous salts. Thus ferric sulphate is reduced to ferrous sulphate, and ferric chloride to ferrous chloride—

$$Fe_2(SO_4)_3 + SO_2 + 2\,H_2O = 2\,FeSO_4 + 2\,H_2SO_4.$$
$$2\,FeCl_3 + SO_2 + 2\,H_2O = 2\,FeCl_2 + H_2SO_4 + 2\,HCl.$$

Potassium permanganate and potassium chromate are also readily reduced, the change being rendered conspicuous by the alterations in colour which result, the purple permanganate being decolorised, and the yellow chromate turned green.

Exp. 155.—Add a solution of sulphur dioxide in water to solutions of potassium permanganate and potassium chromate respectively. Note the colour changes; they may be used as tests for sulphur dioxide, both in the gaseous state and in solution. Potassium chromate is more usually employed for this purpose than potassium permanganate.

226. **How to work out an Equation.**—It will be useful to discuss the mode of arriving at the equations which express the reactions taking place. Taking the case of potassium permanganate we know that the substances we start with are $KMnO_4$, SO_2, and water, and the products are acid potassium sulphate, $KHSO_4$ (not the normal sulphate, because free sulphuric acid is produced), manganese sulphate, $MnSO_4$, and free sulphuric acid. Now potassium permanganate may be considered as made up of the two oxides, K_2O and Mn_2O_7 ($K_2O + Mn_2O_7 = K_2Mn_2O_8 = 2\ KMnO_4$), and manganese sulphate of MnO and SO_3. We may therefore represent the reduction of potassium permanganate to manganese sulphate by reference to the corresponding oxides of manganese, thus—

$$Mn_2O_7 \rightarrow 2\ MnO + 5O.$$

But Mn_2O_7 corresponds to two molecules of potassium permanganate, and therefore *two molecules of* $KMnO_4$ *yield five atoms of oxygen available for oxidising purposes*, i.e. of so-called "available oxygen." Now, one molecule of sulphur dioxide requires one atom of oxygen to convert it into sulphur trioxide, the oxide corresponding to sulphuric acid; consequently 5 atoms of oxygen will oxidise 5 molecules of sulphur dioxide. We can now write down the left-hand side of the equation with the exception of an unknown quantity of water, say x molecules—

$$2\ KMnO_4 + 5\ SO_2 + xH_2O =$$

Now since the potassium goes to $KHSO_4$ and the manganese to manganese sulphate, the right-hand side of the equation may be written—

$$= 2\ KHSO_4 + 2\ MnSO_4 + yH_2SO_4,$$

where y has to be determined.

It is easy to see that $y = 1$, for only one atom of sulphur of the 5 SO_2 remains to be accounted for. So far then we may write the equation—

$$2\ KMnO_4 + 5\ SO_2 + xH_2O = 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4.$$

But on the right side of the equation we have four atoms of hydrogen, and in order that the left-hand side may have the same number we must make $x = 2$. The correct equation is, therefore—

$$\underset{\text{Violet.}}{2\ KMnO_4} + 5\ SO_2 + 2\ H_2O = 2\ KHSO_4 + \underset{\substack{\text{Colourless}\\\text{(in dilute solution).}}}{2\ MnSO_4} + H_2SO_4.$$

In the case of potassium chromate there is not enough sulphuric acid produced to convert all the potassium and chromium into sulphates, so that some free sulphuric acid must be added. Reasoning in a similar manner to that adopted above the equation representing the reaction is found to be—

$$\underset{\text{Yellow.}}{2\ K_2CrO_4} + 3\ SO_2 + 2\ H_2SO_4 = 2\ K_2SO_4{}^{*} + \underset{\text{Green.}}{Cr_2(SO_4)_3} + 2\ H_2O.$$

227. Action of Sulphur Dioxide on Iodine—Reversible actions.—Iodine is reduced to hydriodic acid by sulphur dioxide in the presence of water, but the reaction ceases when a small quantity of hydriodic acid has been produced, owing to the tendency of the latter to reduce sulphuric acid, *i. e.* for the reaction to proceed in the reverse direction. This is an example of a *reversible action*, the exact course of the reaction depending on the *relative masses* of the reacting substances (other conditions remaining the same).

The direct reaction is thus represented—

$$I_2 + 2\ H_2O + SO_2 = H_2SO_4 + 2\ HI,$$

and the reverse reaction is, of course—

$$H_2SO_4 + 2\ HI = I_2 + 2\ H_2O + SO_2.$$

To indicate that the change is reversible it is often expressed thus—

$$I_2 + 2\ H_2O + SO_2 \rightleftarrows H_2SO_4 + 2\ HI.$$

---

[*] $KHSO_4$ will be produced if *excess* of sulphuric acid is added.

When the direct and inverse reactions are proceeding at the same rate no further change will apparently take place, though there is no reason for supposing that the reactions cease altogether; they merely continue at equal rates, some molecules of iodine being reduced, whilst some molecules of hydriodic acid are oxidised.

Exp. 156.—Liberate iodine from potassium iodide by adding a *few drops* of chlorine water; now add an aqueous solution of sulphur dioxide, and the brown colour of the iodine will disappear.

228. **Composition of Sulphur Dioxide**.—This may be determined by synthesis. By means of the arrangement shown (Fig 58) a fragment of sulphur may be burnt in oxygen. The sulphur is in contact with a thin piece of platinum wire through which an electric current is passed; this heats the wire and so ignites the sulphur. The apparatus and the oxygen used in the experiment must be free from moisture. The gas in the globe at first expands owing to the heat of combustion, and forces the mercury up the further limb, but on cooling it returns to its original volume. It is seen therefore, that during the combination of sulphur and oxygen to form sulphur dioxide no alteration in volume occurs, that is to say, ***sulphur dioxide contains its own volume of oxygen.*** It follows then from Avogadro's hypothesis

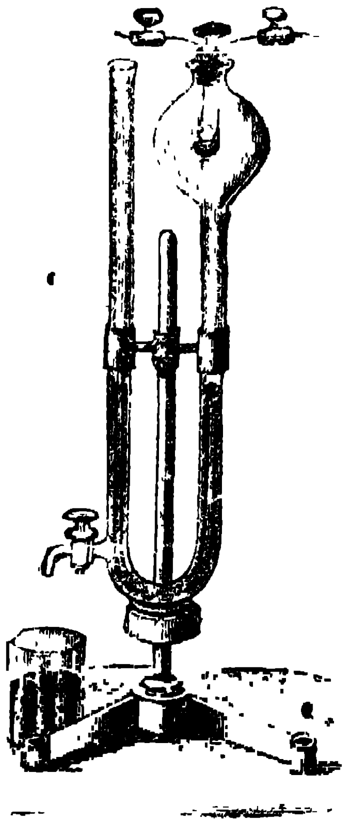

FIG. 58.

that one molecule of sulphur dioxide must contain one molecule of oxygen. Further, since the molecular weight of the gas as found from its density is 64, the composition, deduced by a method similar to that used for sulphuretted hydrogen (see § 221), must be represented by the formula SO_2.

229. **Sulphurous Acid and Sulphites.**—We have seen that sulphur dioxide dissolves readily in water, forming an acid, H_2SO_3. This acid has never been isolated from its dilute aqueous solution, any attempt to concentrate the solution resulting in decomposition with loss of sulphur dioxide. Sulphurous acid contains two atoms of hydrogen in its molecule, both of which are replaceable by metals, it is, therefore, a *dibasic* acid (see § 87), and gives rise to two series of salts called *sulphites*. The first series in which both atoms of hydrogen are replaced are the *normal* sulphites, *e.g.* Na_2SO_3, K_2SO_3, $CaSO_3$; the second series in which only one hydrogen atom is replaced are the *acid* sulphites, *e.g.* $NaHSO_3$, $KHSO_3$, $CaH_2(SO_3)_2$. $NaHSO_3$ is called by three different names, viz. acid sodium sulphite, sodium hydrogen sulphite, and bisulphite of soda; the second regards sulphurous acid as a hydrogen salt, the third is a popular name which has no scientific basis.

The sulphites of the alkali metals may be prepared by passing sulphur dioxide into solutions of the corresponding hydroxides or carbonates.

Exp. 157.—Take 50 c.c. of a solution of caustic soda, and pass sulphur dioxide into it till it is saturated with the gas. On allowing the solution to evaporate at ordinary temperatures (it decomposes when heated), or on adding alcohol to it, the *acid salt*, sodium hydrogen sulphite, separates out—

$$NaOH + SO_2 = NaHSO_3.$$

If we add a second 50 c.c. of the same solution of caustic soda we shall then obtain on evaporation or treatment with alcohol the *normal* salt—

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

In a similar way, substituting caustic potash for caustic soda, the sulphites of potash may be prepared. The normal sulphites of all metals excepting the alkali metals are insoluble in water, and may be obtained as precipitates by the addition of a soluble salt of the metal to a solution of an alkaline sulphite—

$$CaCl_2 + Na_2SO_3 = CaSO_3 + 2\ NaCl.$$

Sulphites slowly take up oxygen from the air, passing into sulphates, and all sulphites are decomposed by acids with evolution of SO_2.

SULPHUR TRIOXIDE, SO_3.

230. This body occurs in small quantity with the sulphur dioxide formed during the combustion of sulphur or iron pyrites.

Preparation.—Sulphur dioxide and oxygen are passed over platinum sponge, obtained by igniting the double chloride of ammonium and platinum. The gases must be dry, and the platinum sponge gently heated, and there then appear at the exit dense white fumes, which if passed into a cool dry receiver condense to white silky needles of sulphur trioxide.

A second method which is employed in the production of sulphur trioxide in large quantities is based on the decomposition of ferrous sulphate, $FeSO_4 \cdot 7\ H_2O$. This body, when heated, first loses most of its water of crystallisation. The partially dehydrated salt more strongly heated is decomposed thus—

$$2\ FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

The water which still remains attached to the salt, however, combines with some of the SO_3 forming H_2SO_4, and this takes up another molecule of SO_3 forming $H_2S_2O_7$—

$$H_2O + SO_3 = H_2SO_4 \text{ and } H_2SO_4 + SO_3 = H_2S_2O_7.$$

The acid thus produced is known as Nordhausen sulphuric acid; it differs from ordinary sulphuric acid, in that it fumes when exposed to moist air, and is often termed *fuming sulphuric acid.* This liquid, which condenses from the distillation of partially dehydrated ferrous sulphate, when removed from the receiver and heated, yields the SO_3 which it has taken up, leaving behind sulphuric acid—

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

By distilling with a powerful dehydrating agent, such as phosphorus pentoxide, the elements of water may even be removed from sulphuric acid itself, and this affords a third method whereby SO_3 may be obtained—

$$P_2O_5 + H_2SO_4 = 2\ HPO_3 + SO_3.$$

231. **Properties of Sulphur Trioxide.**—At ordinary temperatures sulphur trioxide forms white transparent needles, which melt at 15° C., and boil at 46° C.; at a red heat it breaks up into sulphur dioxide and oxygen. It combines very eagerly with water, evolving much heat, and in contact with water it gives a hissing sound like that of the quenching of hot iron; sulphuric acid is thereby formed. It is of interest to add that sulphur trioxide enters into direct combination with certain metallic oxides, with the production of the corresponding sulphates; for instance, when baryta, BaO, and sulphur trioxide are mixed they combine to form barium sulphate, $BaSO_4$, and so much heat is evolved that the mass becomes incandescent.

SULPHURIC ACID, H_2SO_4.

232. **Manufacture.**—We have seen that under certain circumstances sulphur dioxide combines with oxygen to form sulphur trioxide, and that this in presence of water gives sulphuric acid. We have also seen that the oxidation of sulphurous acid to sulphuric acid takes place slowly when its aqueous solution is exposed to air at ordinary temperatures.

Such methods are, however, not suitable for the production of large quantities* of sulphuric acid as an article of commerce.

The oxidation of sulphurous acid is effectually performed by the intervention of the oxides of nitrogen, and on the large scale sulphur dioxide, oxygen (supplied in the form of air) and steam are brought together, and these in presence of oxides of nitrogen form sulphuric acid.

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time—

$$2\ FeS_2 + 11\ O = Fe_2O_3 + 4\ SO_2.$$

The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chili saltpetre, $NaNO_3$—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3\ ;$$

the acid fumes are carried into the flues along which the sulphur dioxide, and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary.

The *steam* is supplied from low pressure boilers, and introduced into the "chambers" in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of contact between the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually three in number, and have a total capacity of 100,000 to 150,000 cubic feet, the relation of the sulphur burnt to the capacity of the chamber being such that the average-time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all

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* Over a million tons of oil of vitriol are produced in Great Britain alone in the course of a year.

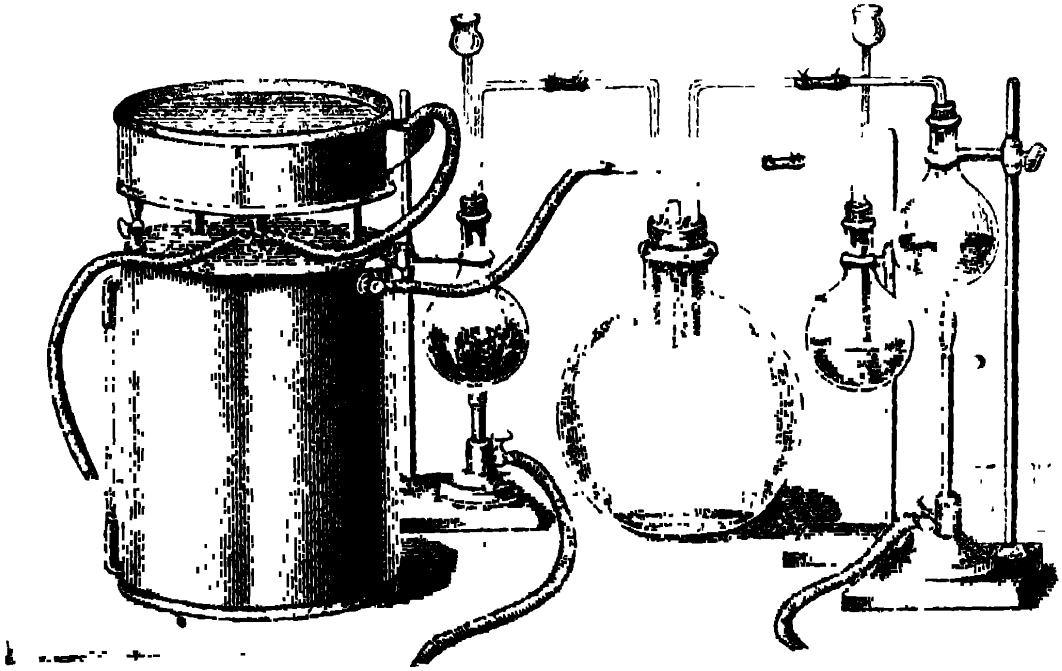

FIG. 59.

by sulphuric acid of the strength produced in the chambers. The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

233. Laboratory representation of the Sulphuric Acid Manufacture.—The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

(1) Sulphur dioxide (for preparation see § 223),
(2) Nitric oxide („ „ „ § 203),
(3) Steam,
(4) Oxygen from a gasholder;

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in Fig. 59.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply; crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current of oxygen, and then passing in more steam, these crystals will dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid (see § 237).

234. **The theory of the Sulpnuric Acid Manufacture.**—As we have seen (§ 225), sulphur dioxide under the action of air and moisture is transformed into sulphuric acid, but the change takes place very slowly, and the sulphuric acid obtained is extremely dilute. In presence of certain substances, notably the higher oxides of nitrogen as in the sulphuric acid chambers, the conversion is more rapid: but much difference of opinion exists as to the actual changes which take place, and even as to the particular oxides of nitrogen which take part in the reaction.

The older theory, originally suggested by Berzelius, regards the nitric oxide (NO) as the body which brings about the formation of the sulphuric acid. This it does by taking up oxygen from the air and forming nitrogen peroxide (NO_2), which in its turn oxidises the sulphur dioxide, and in presence of steam forms sulphuric acid, being itself reduced again to nitric oxide, the alternate oxidation and reduction going on indefinitely—

$$(1)\ NO_2 + SO_2 + H_2O = NO + H_2SO_4.$$
$$(2)\ 2\,NO + O_2 = 2\,NO_2.$$

It is however observed that if the chambers are insufficiently supplied with steam, white crystals ("lead chamber crystals") are formed, consisting of nitrosulphonic acid,

$SO_2(OH)(NO_2)$. According to the above theory the formation of nitrosulphonic acid is not essential to the process, and does not occur in chambers working normally.

The theory more recently proposed by Lunge, on the other hand, assumes nitrogen trioxide * to be the true intermediary in the formation of sulphuric acid, and nitrosulphonic acid to be continually formed in the chambers and decomposed again by the excess of steam according to the equations—

$$(3)\ 2\,HNO_3 + 2\,SO_2 + H_2O = 2\,H_2SO_4 + N_2O_3.$$

$$(4)\ N_2O_3 + O_2 + 2\,SO_2 + H_2O = 2\,SO_2(OH)(NO_2).$$

$$(5)\ 2\,SO_2(OH)(NO_2) + H_2O = N_2O_3 + 2\,H_2SO_4.$$

Under some conditions, and especially where the gases are just entering the chambers and sulphur dioxide is in large excess, it is, however, admitted that nitric oxide plays a prominent part. With this exception Lunge's theory is not inconsistent with the observations recorded in actual working on the large scale.

235. **Properties of Sulphuric Acid.**—The pure concentrated acid is a thick oily liquid (sp. gr. 1·84), from whence it derives the name, *oil* of vitriol. It boils at 338° C., with partial decomposition, so that when the acid containing 100 per cent. H_2SO_4 is distilled the residue becomes weaker, until it reaches a strength of about 98·5 per cent. H_2SO_4, at which it remains constant.

It is highly corrosive, charring wood and many organic substances even at the ordinary temperature. This is largely owing to the great avidity with which it takes up water. Wood consists mainly of cellulose, a compound of carbon, hydrogen and oxygen in the proportions in which they are contained in water: the acid therefore abstracts water, leaving a mass of carbon.

The methods of preparation of two common gases, ethylene and carbon monoxide, depend upon this same property (see Chaps. XXI, XXIII), as does also the employment of concentrated sulphuric acid for drying gases. When sulphuric acid and water are mixed a large amount of heat is evolved, again showing the great affinity they possess for one another, and at the same time there is a considerable diminution in volume. The contraction reaches a maximum, viz. 8 per cent. of the sum of the volumes of acid and water, when the ratio of acid to water corresponds to a hydrate of the formula $H_2SO_4 \cdot 2H_2O$; this probably has a definite existence.

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* The theory holds if N_2O_3 be regarded as a mixture of NO_2 and NO (see § 202).

When sulphuric acid vapour is heated to a temperature of about 450° C. it is almost completely dissociated into water and sulphur trioxide; this is shown by the fact that the vapour density is only half what it should be if the molecules consisted of H_2SO_4.

The following considerations will show that the low value of the vapour density proves that dissociation has taken place. Since each molecule of sulphuric acid gives two molecules on dissociation, one of H_2O and one of SO_3, it follows from Avogadro's hypothesis that the volume of the dissociation products will be double the volume of the sulphuric acid from which they are derived (on reduction to standard conditions). Consequently the vapour density will be half the theoretical value, which agrees with the experimental result stated above.

When the mixture of water and sulphur trioxide obtained by heating sulphuric acid vapour has its temperature still further raised the sulphur trioxide breaks up into sulphur dioxide and oxygen. Thus, when sulphuric acid is dropped on red-hot bricks it decomposes, as represented in the following equation—

$$2\ H_2SO_4 = 2\ H_2O + 2\ SO_2 + O_2.$$

This fact has been utilised as a means of manufacturing oxygen from sulphuric acid on the large scale.

Sulphuric acid is an oxidising agent, though a much weaker one than nitric acid, as we should expect from the smaller percentage of oxygen it contains and the very much higher temperature required to break it up with separation of free oxygen. Thus it is only when *hot and concentrated* that sulphuric acid exhibits oxidising properties. We have already (§ 223) met with examples of the oxidation of both metals (copper and mercury) and non-metals (carbon and sulphur) by sulphuric acid; most of the remaining metals and some other non-metals are also oxidised by the hot strong acid.

236. **Action of Sulphuric Acid on Metals.**—*Dilute* sulphuric acid dissolves some metals, such as zinc, iron, and magnesium, with formation of a sulphate of the metal and hydrogen.

Concentrated sulphuric acid has practically no action on common metals in the cold, a few bubbles only of hydrogen being produced. When warmed, however, it reacts with most metals, producing sulphates of the metals and sulphur dioxide mixed with hydrogen; in the cases of copper and nickel some subsulphide is produced at the same time. As a type of the reaction which takes place between a metal and strong sulphuric acid, we may write the equation which expresses the main result of the interaction of copper and sulphuric acid, viz.—

$$Cu + 2\ H_2SO_4 = CuSO_4 + 2\ H_2O + SO_2.$$

As regards the actual *modus operandi* of the reaction two explanations have been advanced. The first suggests that the primary reaction is the formation of a sulphate of the metal and hydrogen. The hydrogen being in the nascent state, oxidises itself at the expense of the oxygen of the sulphuric acid, forming water and sulphur dioxide thus—

$$\left\{\begin{array}{l} Cu + H_2SO_4 = CuSO_4 + \underset{\text{Nascent.}}{2\ H}, \\ \underset{\text{Nascent.}}{2\ H} + H_2SO_4 = SO_2 + 2\ H_2O. \end{array}\right.$$

The second explanation suggests that the primary action is the oxidation of the metal by the acid, and that this is followed by solution of the oxide in an excess of acid. Thus—

$$\left\{\begin{array}{l} Cu + H_2SO_4 = CuO + H_2O + SO_2, \\ CuO + H_2SO_4 = CuSO_4 + H_2O. \end{array}\right.$$

In the following table a *résumé* of the action of sulphuric acid on the common metals is given; the gaseous products are not mentioned because, in all cases, with *cold dilute* acid hydrogen is evolved, and with *hot concentrated* acid sulphur dioxide (with some hydrogen).

Metal.	Products with cold dil. H_2SO_4	Products with hot conc. H_2SO_4
Magnesium	$MgSO_4$	$MgSO_4$
Zinc	$ZnSO_4$	$ZnSO_4$
Iron	$FeSO_4$	$Fe_2(SO_4)_3$
Cadmium	$CdSO_4$	$CdSO_4$
Mercury	No action	Hg_2SO_4 (Hg in excess) $HgSO_4$ (H_2SO_4 in excess)
Lead	No action	$PbSO_4$ (action slow)
Copper	No action in absence of air	$CuSO_4$ and Cu_2S
Tin	No action	$SnSO_4$
Silver	No action	Ag_2SO_4
Aluminium	No action	$Al_2(SO_4)_3$
Bismuth	No action	$Bi_2(SO_4)_3$
Nickel	$NiSO_4$ (action slow)	$NiSO_4$ and NiS
Antimony	No action	$Sb_2(SO_4)_3$
Gold	No action	No action
Platinum	No action	No action

237. The Sulphates.—These are the salts produced by the replacement of the hydrogen in sulphuric acid by metals. They are produced by the action of sulphuric acid on the metals (in some cases), or on metallic oxides, hydroxides, or carbonates. They may also be prepared by evaporating the salts of the more volatile acids, such as hydrochloric and nitric acids, to dryness with sulphuric acid; the more volatile acid is driven off and a sulphate of the metal is formed.

Three crystalline sulphates which have long been known, *i.e.* ferrous sulphate, $FeSO_4 \cdot 7\,H_2O$, copper sulphate, $CuSO_4 \cdot 5\,H_2O$, and zinc sulphate, $ZnSO_4 \cdot 7\,H_2O$, were called respectively green, blue, and white *vitriol*, from their colours and the glassy transparency of their crystals (L. *vitreum*, glass). Sulphuric acid was originally called *oil of* *vitriol*, because it was obtained by the distillation of green vitriol.

The sulphates are remarkable for their tendency to form well-defined crystalline double sulphates, *e.g.* alum, $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\ H_2O$.

Insoluble Sulphates may be obtained by mixing a solution of a soluble salt of the metal whose sulphate is required with a solution of a soluble sulphate, when double decomposition takes place with precipitation of the insoluble salt. The sulphates of lead, calcium, barium and strontium are insoluble or only slightly soluble in water, the rest being readily soluble.

Sulphuric acid, like sulphurous acid, is a dibasic acid and forms two classes of sulphates, the *normal* sulphates such as Na_2SO_4, $CaSO_4$, and the *acid* sulphates such as $NaHSO_4$, either one or the other being formed according to whether the base or the acid is in excess.

Test for Sulphates.—

Exp. 158.—Add barium chloride to a solution which contains either sulphuric acid or a sulphate in presence of hydrochloric acid: a white precipitate is formed consisting of sulphate of barium. This is the only common barium salt which is insoluble in water and acids, and the formation of the precipitate is therefore characteristic, and may be taken as a sure indication of the presence of sulphuric acid either in the free state or in combination.

238. **Uses of Sulphuric Acid.**—Sulphuric acid is the most important of all the acids. It is very largely used in the manufacture of other acids, such as nitric and hydrochloric acids, in the manufacture of salt-cake—the first stage in the Leblanc process for the manufacture of washing-soda—and in the conversion of normal calcium phosphate, $Ca_3(PO_4)_2$, into the acid calcium phosphate, $CaH_4(PO_4)_2$; the latter is much used for agricultural purposes as a fertiliser, because it is soluble in water, whereas the normal salt is insoluble and so cannot be assimilated by plants. As already mentioned, sulphuric acid is used in the laboratory for drying gases and for the preparation of such gases as

carbon monoxide and ethylene. It is also largely employed in making *storage cells* or *accumulators* for the generation of electric currents.

THIOSULPHURIC ACID, $H_2S_2O_3$.

239. Free thiosulphuric acid may be obtained in dilute solution by the action of a mineral acid on a thiosulphate, but it is very unstable, undergoing decomposition according to the equation—

$$H_2S_2O_3 = H_2O + SO_2 + S.$$

The *thiosulphates* may be obtained by boiling solutions of sulphites with sulphur when direct combination takes place—

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + S = \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3}.$$

The sodium salt is the most important; it is generally incorrectly called "hyposulphite of soda" or merely "hypo." It is much used in photography on account of the power it possesses of dissolving the haloid salts of silver, a soluble double thiosulphate of silver and sodium being formed—

$$AgCl + Na_2S_2O_3 = NaCl + \underset{\text{Sodium silver thiosulphate.}}{AgNaS_2O_3}.$$

Sodium thiosulphate is also used to remove the last traces of chlorine from a fabric which has been bleached, such a substance being termed an *anti-chlor.* This action depends upon the ease with which it is oxidised to sodium sulphate—

$$Na_2S_2O_3 + H_2O + Cl_2 = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + 2\,HCl + S.$$

Test for Thiosulphates.—Thiosulphates in solution are distinguished from sulphites by the fact that with dilute mineral acids they give off sulphur dioxide and also *form a precipitate of finely-divided sulphur*—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + SO_2 + S + H_2O.$$

QUESTIONS.—CHAPTER XIX.

1. Describe how sulphur dioxide is prepared on the laboratory scale and how it is collected.
2. State the *physical* properties of sulphur dioxide. What volume of the gas will dissolve in 100 c.c. of water at 10° C. under normal pressure?
3. Explain the bleaching action of sulphur dioxide, and show in what respects it differs from that of chlorine.
4. What is the effect of passing chlorine into a solution of sulphur dioxide in water? Give the equation.
5. Express by equations the action of sulphur dioxide on solutions of (1) ferric sulphate, (2) potassium permanganate in the presence of sulphuric acid, (3) potassium chromate in the presence of sulphuric acid.
6. Explain how the equation expressing a complex chemical change (*e. g.* the action of sulphur dioxide on potassium permanganate in the presence of sulphuric acid) may be built up.
7. What is meant by a *reversible action?* Discuss an example.
8. A little chlorine is passed into a solution of potassium iodide, and then afterwards sulphur dioxide is passed in; state the changes which take place and give equations representing them.
9. "Sulphur dioxide contains its own volume of oxygen." Explain the meaning of this statement, and show how you would prove the truth of it by experiment.
10. Describe the preparation of the normal and acid sulphites of soda; what is the action of sulphuric acid on them?
11. Under what circumstances does sulphur dioxide combine directly with oxygen?
12. What is the action of heat on $FeSO_4$, $7\ H_2O$?
13. How may sulphur trioxide be obtained from (*a*) Nordhausen sulphuric acid; (*b*) ordinary sulphuric acid?

14. Describe how sulphur dioxide becomes transformed into sulphuric acid on the large scale; give equations.
15. How is sulphur dioxide obtained for the manufacture of sulphuric acid, and what means are employed to ensure its being mixed with the proper quantity of air?
16. Discuss the action of heat on sulphuric acid.
17. Compare the reactions between the metals, zinc, mercury and iron respectively, and (1) dilute sulphuric acid, (2) hot concentrated sulphuric acid.
18. What explanations of the action of hot strong sulphuric acid on copper have been suggested?
19. Write down the formulæ of the normal sulphates of copper, potassium, lead, iron and aluminium.
20. Give a method of testing for the presence of a soluble sulphate, and show how you would distinguish whether an aqueous solution contained—
    (*a*) free sulphuric acid only,
    (*b*) a normal sulphate,
    (*c*) a mixture of the two.
21. What are the chief uses of sulphuric acid?
22. What is the correct name for "hyposulphite of soda"? How is this substance prepared, and what are its properties and uses?

CHAPTER XX.

PHOSPHORUS.

240. Occurrence.—Phosphate of lime, $Ca_3(PO_4)_2$, the principal source of phosphorus, forms the essential constituent of the mineral apatite, and of bone-ash. The former occurs in the older formations of the earth's crust as—

Chlorapatite, $3\ Ca_3(PO_4)_2 \cdot CaCl_2$;
and Fluorapatite, $3\ Ca_3(PO_4)_2 \cdot CaF_2$.

Bone-ash is obtained by the dry distillation of bones.

In small quantities phosphates are very widely distributed; all fertile soils contain a small percentage, and they are always found in plants, being, like nitrogen, essential to plant-life.

241. Manufacture of Phosphorus.—The first step in the manufacture of phosphorus from bone-ash consists in treating it with sulphuric acid, whereby a double decomposition takes place—

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 = 3\ CaSO_4 + 2\ H_3PO_4.$$

When the decomposition is complete, the product is filtered through cinders; the calcium sulphate remains on the filter, and the phosphoric acid passes through.

The liquid is then concentrated, mixed with charcoal, and further heated almost to dryness, the H_3PO_4 losing water and being converted into HPO_3—

$$H_3PO_4 \quad HPO_3 + H_2O.$$

Finally, the granular product is heated to full redness in clay retorts placed horizontally in series over a fire, when the following reaction takes place—

$$2\,HPO_3 + 6\,C \quad H_2 + 6\,CO + 2\,P.$$

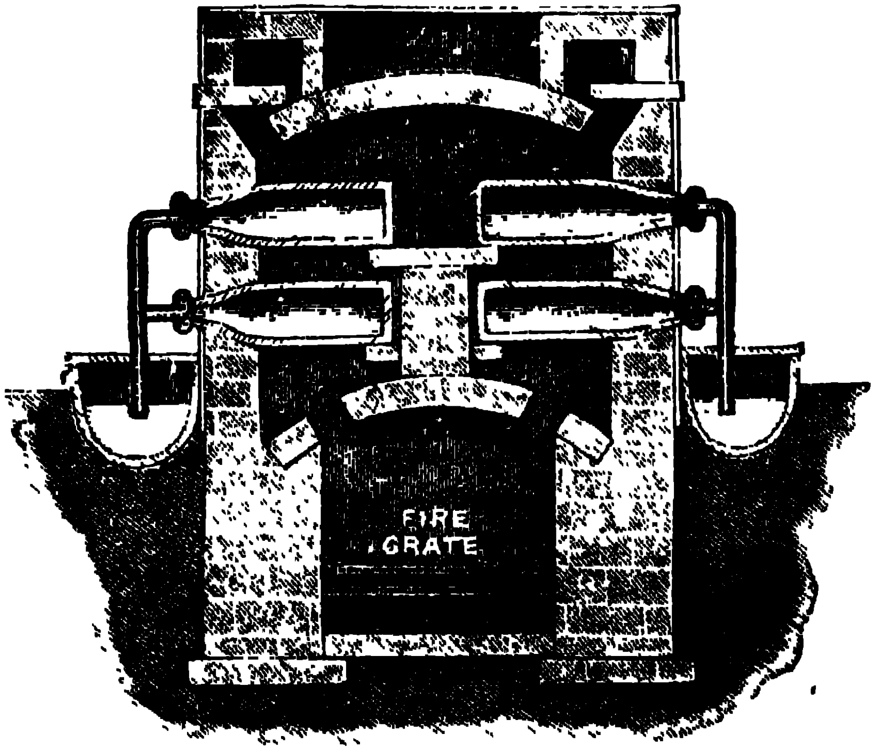


FIG. 60.

Luted into the mouth of each retort is an iron pipe, bent at right angles and dipping into water; the vapour of phosphorus is thus led into the water, and there condensed out of contact with air. The temperature of the water is high enough to keep the phosphorus in the liquid state, and it can be run off or ladled out from time to time. It is further refined by re-melting in water, and filtering through chamois leather or canvas to remove suspended matter, and then finally cast into sticks.

242. **Properties of Phosphorus.**—The phosphorus so obtained is a yellowish, translucent, crystalline solid which can be readily cut with a knife. It has a specific gravity of 1·82, it melts at 43° C., and boils at 269° C. It is insoluble in water, but readily dissolves in bisulphide of carbon.

When phosphorus is exposed to the air it slowly oxidises and emits white fumes (visible in the dark) consisting of a number of oxidation products, namely, phosphorous oxide (P_4O_6), phosphorous acid (H_3PO_3), phosphorus pentoxide (P_4O_{10}), phosphoric acid (H_3PO_4), and hypophosphoric acid ($H_4P_2O_6$). At the same time the phosphorus becomes faintly luminous. The cause of this luminosity has not been established with certainty, but it is probably connected in some way with the presence of ozone; this substance (along with hydrogen peroxide) is always produced during the slow oxidation of phosphorus, and it has been found that in the presence of bodies such as ether and turpentine, which destroy ozone, the luminosity ceases. At 34° C. phosphorus ignites in air and burns with great brilliancy, forming phosphorus pentoxide, P_4O_{10}. On account of the ease with which phosphorus undergoes oxidation it must be kept under water. It should be mentioned that *perfectly dry air* (or oxygen) has no action on phosphorus.

Phosphorus combines also at ordinary temperatures with fluorine, chlorine, bromine, iodine and sulphur, and in the finely-divided condition with oxygen, with the evolution of light and heat.

Phosphorus may be obtained in two other allotropic modifications, red phosphorus, and the recently discovered scarlet phosphorus.

243. **Red Phosphorus** is, according to its method of preparation, a reddish-brown powder or a close-textured mass showing conchoidal fracture. This form is prepared on the large scale by heating ordinary phosphorus at 250° C. in cast-iron pots to which air has only limited access, and removing the unconverted phosphorus which remains by boiling the finely-divided product with caustic

soda solution. On a small scale in the laboratory it may readily be obtained by heating ordinary phosphorus in an atmosphere of nitrogen or carbon dioxide. The amorphous phosphorus differs very considerably in its properties from that already described. It has a higher specific gravity (2·24), and is insoluble in bisulphide of carbon. It undergoes no change in air at ordinary temperatures, and may be freely handled without danger; it combines with oxygen, the halogens, and sulphur at much higher temperatures than ordinary phosphorus. Unlike ordinary phosphorus, it is not poisonous. Red phosphorus was formerly called "amorphous" phosphorus, but it has recently been shown to possess a crystalline structure.

Lucifer matches are tipped with a mixture of phosphorus and certain substances, such as lead dioxide and potassium nitrate, which readily part with oxygen. "Safety" matches contain no phosphorus, being tipped with a mixture of antimony sulphide (Sb_2S_3), the sulphur being the inflammable body, and potassium chlorate; in this case the match is ignited by rubbing it on a prepared surface of red phosphorus and powdered glass. In either case the heat requisite to promote chemical action and to ignite the phosphorus is generated by friction on a rough surface.

Scarlet Phosphorus.—This form of phosphorus which has been obtained recently is apparently an amorphous modification of the element.

Hydrides of Phosphorus.

244. Phosphorus forms three hydrides—

Gaseous phosphoretted hydrogen or phosphine	PH_3.
Liquid phosphoretted hydrogen	P_2H_4.
Solid phosphoretted hydrogen	P_4H_2.

The only one of these compounds which we shall consider is the gaseous hydride PH_3, the others being unimportant.

Phosphorus Trihydride, or Phosphine, PH_3.

245. **Preparation.**—This gas, which is the analogue of ammonia, is obtained by heating phosphorus in a flask with a solution of caustic soda. As obtained in this way it is mixed with small quantities of the liquid and solid hydrides, which render it spontaneously inflammable in air; so, to prevent the gas taking fire in the flask, the air is, previous to heating, displaced from the apparatus by coal gas. The end of the delivery tube dips under water as shown in Fig. 61, and as each bubble of gas reaches the surface it inflames and produces a ring of white smoke (phosphorus pentoxide).

The reaction which takes place is—

$$4\,P + 3\,NaOH + 3\,H_2O = \underset{\text{Sodium hypophosphite.}}{3\,NaH_2PO_2} + PH_3.$$

Phosphine is also formed, along with a considerable quantity of liquid phosphoretted hydrogen, when phosphide of calcium (obtained by heating together lime and phosphorus in a closed crucible) is brought into contact with water.

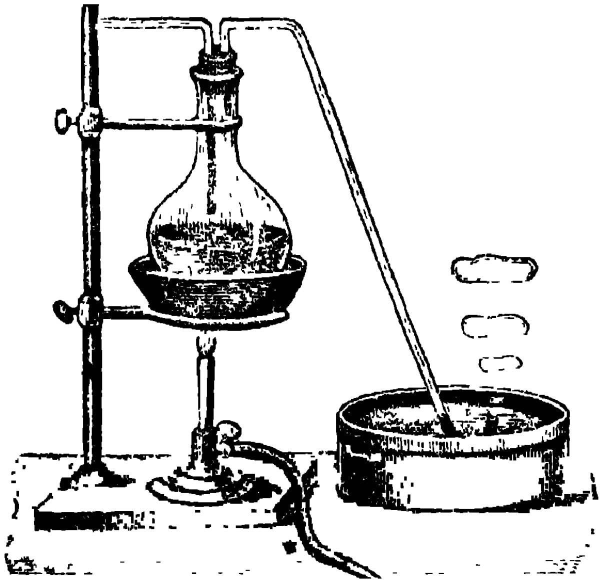


FIG. 61.

Pure phosphorus trihydride is prepared by warming phosphonium iodide, PH_4I (see below), with caustic potash or soda, the reaction being analogous to that employed in the preparation of ammonia—

$$PH_4I + NaOH = PH_3 + NaI + H_2O.$$
$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

The gas may be collected over water.

246. **Properties of PH_3.**—It is a colourless gas which condenses only when cooled to – 90° C. It is very slightly soluble in water, and possesses a penetrating garlic-like odour which is evident even with very small quantities of the gas; it is very poisonous. If free from other hydrides, it is not inflammable in air at ordinary temperatures; heat decomposes the gas into its elements more readily than the corresponding nitrogen compound, NH_3.

Just as ammonia combines directly with the haloid acids HCl, HBr, etc., to form ammonium chloride, ammonium bromide, etc., so phosphorus trihydride forms similar compounds. The combination with hydriodic acid to form phosphonium iodide—

$$PH_3 + HI = PH_4I,$$

takes place very readily.

THE OXIDES AND OXYACIDS OF PHOSPHORUS.

247. A list of the oxides and oxyacids of phosphorus which are known is given in the following table:—

Oxides.	Corresponding Acids.			
P_2O (not known in free state)	Hypophosphorous acid,	H_3PO_2	or	$3\ H_2O \cdot P_2O$.
P_2O_3 (P_4O_6)	Phosphorous acid,	H_3PO_3	or	$3\ H_2O \cdot P_2O_3$.
P_2O_4	Hypophosphoric acid,	$H_4P_2O_6$	or	$2\ H_2O \cdot P_2O_4$.
P_2O_5	Orthophosphoric acid,	H_3PO_4	or	$3\ H_2O \cdot P_2O_5$.
	Pyrophosphoric acid,	$H_4P_2O_7$	or	$2\ H_2O \cdot P_2O_5$.
	Metaphosphoric acid,	HPO_3	or	$H_2O \cdot P_2O_5$.

The more important are phosphorous oxide, P_4O_6, and phosphorus pentoxide, P_2O_5, and the acids derived from them, and we shall restrict ourselves to a study of these compounds.

PHOSPHOROUS OXIDE, P_4O_6.

248. **Preparation.**—Phosphorous oxide is obtained mixed with phosphorus pentoxide when phosphorus is exposed to oxidation in air at ordinary temperature, or when it is burnt in a limited supply of air. Its preparation is carried out in the following manner :—

A glass tube is drawn out into the shape shown at A, Fig. 62, and some pieces of phosphorus are introduced into it. This tube is connected with a metal condenser D, the inner tube of which is provided with a plug of glass wool at the end away from A; the space between the two tubes of the condenser is filled with water. The condenser is attached to a U-tube C connected at its lower end with a bottle E, as shown in the diagram; the U-tube and bottle are surrounded by a freezing mixture of ice and salt. The tube A is gently heated and a current of air is drawn through the apparatus by means of an aspirator attached to the U-tube. The phosphorus melts, but is prevented from running out by the shape of the tube; it burns in the current of air and a mixture of P_4O_6 and P_2O_5 passes over into D, where it condenses. After some time the condenser is heated till the temperature of the water rises to 50° C. as indicated by the thermometer, T. This temperature is sufficient to melt the phosphorous oxide which passes over into the U-tube, where it solidifies, but the phosphorus

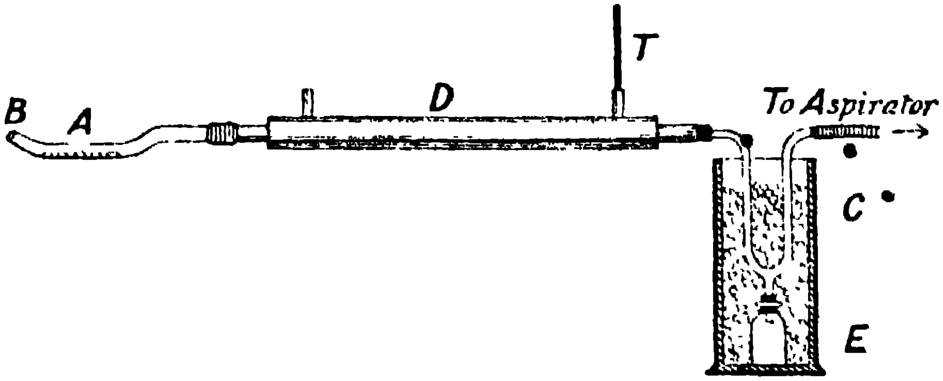


FIG. 62.

pentoxide remains solid and the plug of glass wool keeps it back in D. Occasionally the freezing mixture is removed from the U-tube and bottle, and the U-tube is gently warmed, when the P_4O_6 melts and runs down into bottle.

249. **Properties.**—Phosphorous oxide is a white crystalline solid, melting at 22·5° C. to a colourless liquid. It is slowly dissolved by *cold* water with formation of phosphorous acid, H_3PO_3, and is therefore the anhydride of this acid—

$$P_4O_6 + 6\ H_2O = 4\ H_3PO_3.$$

With *hot* water, however, a violent reaction takes place with formation of red phosphorus, phosphides of hydrogen and phosphoric acid. On exposure to moist air or oxygen it oxidises to phosphorus pentoxide, and if the temperature is slightly raised it takes fire.

The vapour density of phosphorous oxide is 110, and consequently its molecular weight is 2 × 110 = 220. This corresponds to a formula P_4O_6 for the gaseous molecule ($P_4 = 4 \times 31 = 124$, $O_6 = 6 \times 16 = 96$, and $124 + 96 = 220$).

PHOSPHOROUS ACID, H_3PO_3.

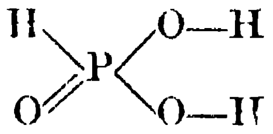
250. **Preparation.**—This acid may be obtained, as already stated, by the action of cold water on phosphorous oxide. It is prepared by the action of water on phosphorus trichloride—

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$

It is not necessary to actually prepare the trichloride, and the most convenient course of procedure is to pass chlorine into phosphorus melted under a layer of water. A solution of phosphorous acid is thus obtained, and on concentrating and allowing to cool, crystals of the acid separate out.

251. **Properties.**—Phosphorous acid is a white, deliquescent crystalline solid, melting at 70° C. Only two of the three hydrogen atoms in the molecule of phosphorous acid

are replaceable by metals, and it is therefore a *dibasic* acid. Thus it forms salts such as KH_2PO_3, K_2HPO_3 and Ag_2HPO_3, but Ag_3PO_3 has not been prepared. Its constitutional formula is probably



i.e. it contains *two* hydroxyl groups—for we have already seen that the basicity of an acid usually depends upon the number of hydroxyl groups it contains.

On heating, phosphorous acid decomposes, yielding phosphoric acid and phosphine—

$$4\ H_3PO_3 = 3\ H_3PO_4 + PH_3.$$

It is a strong reducing agent, as it readily takes up oxygen and is transformed into ordinary phosphoric acid, H_3PO_4. Thus it precipitates metallic copper from a solution of copper sulphate on boiling.

Phosphorus Pentoxide, P_4O_{10}

252. Preparation.—Whenever phosphorus is burnt in an excess of dry oxygen or air this oxide is formed. The operation may be performed in a glass bolt-head with two side tubes, through one of which passes air dried over fused calcium chloride, and through the other the fumes are aspirated, a bottle being placed between the aspirator and the side tube to intercept the phosphorus pentoxide (Fig. 63). A small piece of phosphorus carefully dried

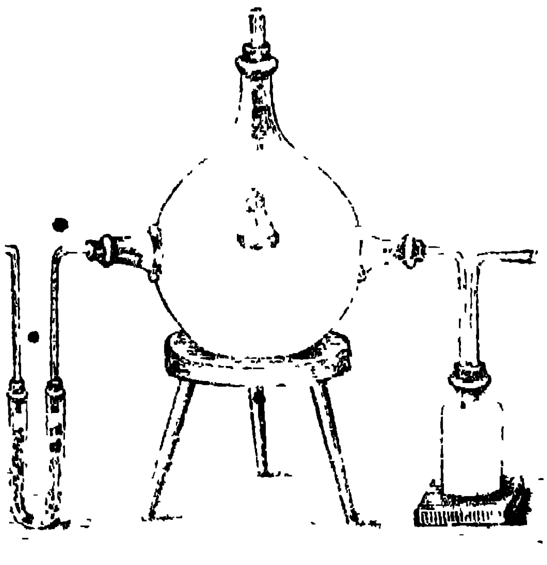


FIG. 63.

between filter paper is introduced through the neck of the bolt-head into a small basin attached as shown, and then successively other pieces, until sufficient of the oxide has been prepared. After the first piece has been ignited by touching it with a hot wire, the basin will be hot enough to start the combustion of the subsequent portions as they are dropped into it. The pentoxide so obtained always contains phosphorous oxide, from which it may be freed by passing it in the gaseous form along with oxygen over gently heated finely-divided platinum. Compare preparation of sulphur trioxide.

253. **Properties of P_4O_{10}.**—The oxide is an amorphous white powder, which when left in contact with moist air gradually absorbs moisture and deliquesces. When thrown into water it combines with it with a hissing noise, and forms metaphosphoric acid, HPO_3—

$$P_4O_{10} + 2\ H_2O = 4\ HPO_3.$$

Its great affinity for water renders it a valuable agent for completely drying gases, whilst in contact with acids it frequently deprives them of water, forming anhydrides—

$$2\ H_2SO_4 + P_4O_{10} = 4\ HPO_3 + 2\ SO_3.$$
$$4\ HNO_3 + P_4O_{10} = 4\ HPO_3 + 2\ N_2O_5.$$

Similarly it chars wood, paper, and many organic substances by its dehydrating action.

ORTHOPHOSPHORIC ACID (*Ordinary Phosphoric Acid*), H_3PO_4.

254. **Preparation.**—Orthophosphoric acid is obtained by dissolving phosphorus pentoxide in water and boiling the solution. It is prepared by the action of nitric acid on ordinary phosphorus, or by boiling for some time a solution of metaphosphoric acid.

Exp. 159.—Introduce about 10 grammes of red phosphorus into a large retort, and cover it with concentrated nitric acid. Place a flask over the mouth of the retort. Now heat cautiously, and presently red fumes of oxides of nitrogen will be evolved by the reduction of the nitric acid—

$$4\ P + 10\ HNO_3 + H_2O = 4\ H_3PO_4 + 5\ NO + 5\ NO_2.$$

Continue the heating in such a manner as to keep the liquid about its boiling-point, but so that as little as possible distils over. When the phosphorus has all disappeared, and red fumes are no longer generated, distil the acid over until that remaining has a syrupy consistency; more red fumes will be evolved at this stage through the oxidation of some phosphorous acid. Finally, transfer the thick liquid to a porcelain dish and evaporate so long as strongly acid fumes (HNO_3) are given off.

As trichloride of phosphorus when treated with excess of water yields phosphorous acid, so the pentachloride, by similar treatment, gives ordinary phosphoric acid—

$$PCl_5 + 4\ H_2O = H_3PO_4 + 5\ HCl.$$

The acid, when sufficiently concentrated, crystallises on standing.

255. **Properties.**—Phosphoric acid is a colourless deliquescent crystalline solid, melting at 41·7° C.; the crystals consist of hard rhombic prisms. It is a tribasic acid, each of the atoms of hydrogen being replaceable by a metal.

256. **The Phosphates.**—The phosphates of the alkali metals sodium, potassium and of ammonium are soluble in water, and are obtained by the addition of the alkaline hydrates to phosphoric acid. The amount of the alkali added may be sufficient to replace one, two, or three atoms of the hydrogen, thus—

$$\underset{40}{NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Sodium dihydrogen phosphate.}}{NaH_2PO_4} + H_2O.$$

$$\underset{80}{2\ NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Disodium hydrogen phosphate.}}{Na_2HPO_4} + 2\ H_2O.$$

$$\underset{120}{3\ NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Normal sodium phosphate.}}{Na_3PO_4} + 3\ H_2O.$$

The numbers underneath show the combining proportions of caustic soda and phosphoric acid required to form such salts. That is to say, if to 98 grammes of phosphoric acid there be added 40 grammes of caustic soda and the solution evaporated the salt NaH_2PO_4 will be obtained; if 80 grammes, then the salt formed will be Na_2HPO_4, and if 120 grammes, the salt Na_3PO_4 will be formed.

Na_3PO_4 is an example of a *normal* salt which is *not neutral* in its reaction with litmus but *alkaline.*

NaH_2PO_4, Sodium dihydrogen phosphate—acid reaction.
Na_2HPO_4, Disodium hydrogen phosphate—slightly alkaline.
Na_3PO_4, Normal sodium phosphate—distinctly alkaline.

The salt ordinarily known as "sodium phosphate" is Na_2HPO_4. It is prepared by adding caustic soda solution to phosphoric acid till the liquid is distinctly alkaline and crystallising the salt. Crystals of the composition $Na_2HPO_4 + 12\ H_2O$ separate out.

The normal phosphates of the alkaline earth metals (Ba, Sr, Ca) and of Mg, Pb, Ag, and indeed of all other metals, are insoluble in water, but soluble in dilute mineral acids. They may be prepared by adding a soluble salt of the metal in question to an aqueous solution of an alkaline phosphate—

$$2\ Na_3PO_4 + 3\ CaCl_2 = Ca_3(PO_4)_2 + 6\ NaCl.$$
$$Na_3PO_4 + 3\ AgNO_3 = Ag_3PO_4 + 3\ NaNO_3.$$

257. **Tests for Phosphates.**—(1) Ferric chloride gives, even in presence of acetic acid, a yellowish-white precipitate of ferric phosphate. (Arsenates give a similar precipitate.)

(2) Silver nitrate gives a pale yellow precipitate of silver phosphate. (Arsenates give a brick-red precipitate.)

(3) Excess of ammonium molybdate in the presence of nitric acid gives a bright yellow precipitate of phosphomolybdate of ammonium even in the cold, but more rapidly on warming. (The arsenates give a similar precipitate only on warming.)

(4) The presence of phosphorus may always be detected by heating a little of the powdered substance along with magnesium filings in a narrow tube and then moistening the product with water. Phosphoretted hydrogen is given off, and may be recognised by its characteristic odour.

258. **Pyrophosphoric Acid, $H_4P_2O_7$,** is obtained as a glassy mass by heating ordinary phosphoric acid to 215° C.—

$$2\ H_3PO_4 = H_4P_2O_7 + H_2O.$$

It is readily soluble in water and in solution is slowly converted into orthophosphoric acid at the ordinary temperature, rapidly on boiling—

$$H_4P_2O_7 + H_2O = 2\ H_3PO_4.$$

As with the phosphates, the salts of the alkali metals are soluble in water, those of the other metals being insoluble in water but soluble in dilute mineral acids.

Tests for Pyrophosphates.—(1) Silver nitrate gives a *white* precipitate of $Ag_4P_2O_7$ (distinction from phosphates).

(2) Pyrophosphoric acid does not coagulate albumen (distinction from metaphosphoric acid).

259. **Metaphosphoric Acid, HPO_3,** is obtained when ortho- or pyrophosphoric acid or their ammonium salts are strongly heated—

$$H_3PO_4 = HPO_3 + H_2O.$$

It is a glassy solid (whence the name *glacial phosphoric acid* by which it is also known) and closely resembles pyrophosphoric acid in appearance. It is readily soluble in water, and in solution passes slowly into orthophosphoric acid; on heating the change takes place rapidly—

$$HPO_3 + H_2O = H_3PO_4.$$

The salts of HPO_3 resemble those of H_3PO_4 and $H_4P_2O_7$ as regards their solubility in water and acids.

Tests for Metaphosphates.—(1) Silver nitrate gives a *white* precipitate of $AgPO_3$ (distinction for phosphates).

(2) Metaphosphoric acid coagulates albumen (distinction from ortho- and pyrophosphoric acids).

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

260. By direct union of phosphorus with these elements, bodies of the type PX_3 and PX_5 are formed, and by the action of moisture on PCl_5 and PBr_5, the oxychloride $POCl_3$, and oxybromide $POBr_3$, respectively, are obtained.

We shall only consider the compounds PCl_3 and PCl_5 in detail; the corresponding compounds of the other halogens closely resemble them in properties.

PHOSPHORUS TRICHLORIDE, PCl_3.

261. **Preparation.**—This compound is prepared by passing dry chlorine over red phosphorus heated in a glass retort; the trichloride distils over and is collected in a receiver cooled by water.

Properties.—Phosphorus trichloride is a colourless mobile liquid boiling at 76° C. It is decomposed by water with formation of phosphorous and hydrochloric acids—

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$

It combines directly with chlorine to form phosphorus pentachloride, and on heating unites with oxygen, forming phosphorus oxychloride, $POCl_3$—

$$PCl_3 + Cl_2 = PCl_5.$$
$$2\ PCl_3 + O_2 = 2\ POCl_3.$$

PHOSPHORUS PENTACHLORIDE, PCl_5.

262. **Preparation.**—Phosphorus pentachloride is prepared by passing chlorine into phosphorus trichloride contained in a flask, using a wide delivery tube, so that the end will not be stopped up by the solid pentachloride.

Properties.—The pentachloride is a light yellow solid, which passes directly into vapour at 168° C., without melting, undergoing partial decomposition into PCl_3 and Cl_2. With a small quantity of water phosphorus pentachloride yields phosphorus oxychloride—

$$PCl_5 + H_2O = POCl_3 + 2\,HCl;$$

but with excess of water phosphoric acid is formed—

$$POCl_3 + 3\,H_2O = PO(OH)_3 + 3\,HCl;$$

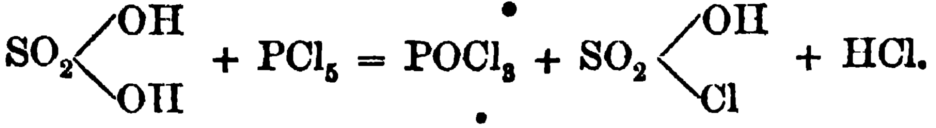
or, writing both stages in one equation—

$$PCl_5 + 4\,H_2O = PO(OH)_3 + 5\,HCl.$$

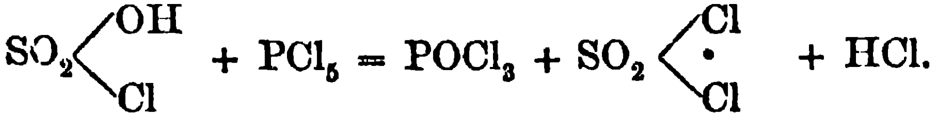
The greater attraction which phosphorus has for oxygen than for chlorine renders both PCl_3 and PCl_5 valuable reagents for substituting chlorine for oxygen or hydroxyl, in the latter case with elimination of HCl; they are much used for this purpose in dealing with carbon compounds. Examples of such actions are given in the following equations:

$$SO_3 + PCl_5 = POCl_3 + SO_2.$$

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$



$$SO_2\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + PCl_5 = POCl_3 + SO_2\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix} + HCl.$$



$$SO_2\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix} + PCl_5 = POCl_3 + SO_2\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + HCl.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_5\cdot OH} + PCl_5 = POCl_3 + \underset{\text{Ethyl chloride.}}{C_2H_5\cdot Cl} + HCl.$$

$$\underset{\text{Acetic acid.}}{C_2H_3O\cdot OH} + PCl_5 = POCl_3 + \underset{\text{Acetyl chloride.}}{C_2H_3O\cdot Cl} + HCl.$$

$$\underset{\text{Aldehyde.}}{CH_3CHO} + PCl_5 = POCl_3 + \underset{\text{Ethylidene chloride.}}{CH_3CHCl_2}.$$

QUESTIONS.—CHAPTER XX.

1. What is the effect of heating chlorapatite and fluorapatite respectively with concentrated sulphuric acid?
2. How is phosphorus extracted from phosphoric acid?
3. Discuss the nature of the changes which take place when phosphorus undergoes slow oxidation in air.
4. Write down in parallel columns the physical properties of ordinary and red phosphorus.
5. What differences are there in chemical behaviour between ordinary and red phosphorus?
6. Why does a match ignite when rubbed on a rough surface? What chemical action takes place during the ignition?
7. To what is the spontaneous ignition of phosphorus trihydride due, and how may the hydride be prepared so as not to ignite spontaneously?
8. Express by equations the action of phosphorus on chlorine, iodine, caustic potash and nitric acid.
9. Compare the trihydride of phosphorus with the trihydride of nitrogen.
10. How is phosphorous oxide prepared, and how may it be converted into the pentoxide?
11. What is the action of (*a*) cold water, (*b*) hot water on phosphorous oxide?
12. How has it been proved that the formula for phosphorous oxide is P_4O_6, not P_2O_3?
13. Describe the preparation and properties of phosphorous acid.
14. How may phosphorus pentoxide be obtained in quantity and converted into metaphosphoric acid and into phosphoric acid?
15. What is the action of water on the trichloride and on the pentachloride of phosphorus? Give equations.
16. Describe in detail the preparation of phosphoric acid from phosphorus.

17. What is meant by saying that orthophosphoric acid is a *tribasic* acid? Write down the names and formulæ of a few phosphates that are soluble in water.
18. By what chemical tests may phosphates be distinguished from arsenates and from pyrophosphates?
19. How are metaphosphoric and pyrophosphoric acids prepared and distinguished?
20. Describe the preparation of the chlorides of phosphorus and of phosphorus oxychloride.
21. 50 grammes of caustic soda are mixed with 61·25 grammes of orthophosphoric acid. What salt will be produced and how much of it will be obtained?

(Na = 23, O = 16, H = 1, P = 31.)

CHAPTER XXI.

CARBON AND THE HYDROCARBONS.

CARBON.

263. CARBON is the first member of a group consisting of the elements carbon, silicon, titanium, zirconium, and thorium, of which the first two members alone come under consideration amongst the non-metals. They show a considerable resemblance to one another in their physical and chemical properties.

Comparing together more particularly carbon and silicon we observe that—

(1) The elements themselves are very infusible.

(2) They exist in allotropic modifications of similar character.

(3) They form oxides of great stability and also gaseous hydrides, CH_4 and SiH_4, the former of these being a stable body, whilst the latter undergoes decomposition very readily.

(4) Carbon and silicon both combine directly with fluorine to form CF_4 and SiF_4 respectively. With the other halogen elements they do not combine directly, but volatile liquid tetrachlorides, CCl_4 and $SiCl_4$, are obtained indirectly.

264. **Occurrence.**—Carbon is found in nature in a state of comparative purity as diamond and graphite, the latter known as mineral plumbago, from which black-lead pencils

are made. These forms do not, however, occur in any very considerable quantity, and the sources from which the large supplies of carbon are obtained are coal and vegetable matter.

The tissue of plants is very constant in composition, and disregarding the moisture and the mineral ash left after combustion, amounting usually to about 1 per cent., *dried wood* is found to consist of

Carbon	50 per cent.
Hydrogen	6 „
Oxygen and nitrogen	44 „

Where plants undergo decay and form thick accumulations of *peat*, the relative proportion of the carbon increases, and the following may be taken as the average composition of peat, leaving out of account moisture and mineral matter—

Carbon	58 per cent.
Hydrogen	5 „
Oxygen and nitrogen	37 „

In deposits of peat and the remains of vegetation which have lain for long periods of time this process of parting with the more volatile constituents and consequent increase in the proportion of carbon goes on, and instead of peat we have a much denser product known as *brown coal* or *lignite*, in which the structure of the vegetation composing it can, however, still be observed. Lignite varies greatly in composition, especially in regard to the amount of moisture and ash. Excluding these, it contains on the average—

Carbon	66 per cent.
Hydrogen	5 „
Oxygen and nitrogen	29 „

In the older formations of the earth's crust there are large deposits of *coal*, which have resulted from long-continued action similar to the foregoing. The seams of coal usually occur at some depth, and are overlaid by other strata. The vegetable tissue from which coal is derived has thus been subjected to immense pressure and to increased temperature, and under these agencies, acting over long periods of time, the changes already noticed in the passage from woody tissue to lignite have been still further accentuated. Coal is darker in colour, denser, and more brittle; as to composition, the following numbers may be compared with those given for wood, peat, and lignite—

	Bituminous coal.	Anthracite.
Carbon	84 per cent.	94 per cent.
Hydrogen	5 „	3 „
Oxygen and nitrogen ...	11 „	3 „

Over 200 million tons of coal are brought to the surface in the United Kingdom annually.

In many localities, especially in South Russia and the United States, there are large deposits of *petroleum*—a mixture of various oils, but all composed of carbon and hydrogen, and hence termed hydrocarbons.

And when we add the very extensive series of carbon compounds which have been prepared in the laboratory from coal and petroleum, and the products, such as starch, sugar, turpentine, albumen, stearin, etc., elaborated by plants and animals, we are in a position to appreciate the immense importance of the element carbon. The study of such bodies is indeed set apart as a special branch of the science, and known as *Organic Chemistry*, or the *Chemistry of the Carbon Compounds.*

Finally, carbon occurs in combination with oxygen as carbon dioxide in the air, and in vast deposits of limestone and dolomite. The carbon dioxide in air, being less than 4 volumes in 10,000, might be regarded as insignificant, but the mass of the atmosphere is such that at this computation there must be very nearly a billion tons of carbon in it.

265. Allotropic Forms of Carbon.—(1) *Diamond* is a crystalline form of carbon; it is found in South Africa and Brazil, usually as octahedra or cubes, or as some modifications of these. Its value is due to its great hardness and brilliancy of lustre, and to the fact that it does not oxidise or undergo change even in presence of corrosive substances. It is the densest form of carbon, having a specific gravity of about 3·5, and is also the most difficult to ignite in oxygen.

It is therefore not to be wondered at that the composition of diamond remained unknown until the time of Lavoisier, although it had been previously observed that diamond could be burnt and left no appreciable residue. Lavoisier about a century ago, by means of a burning glass, ignited diamond in air enclosed over mercury, and found that when it burnt, the gas which was formed turned lime-water milky and was carbon dioxide. Dumas, later, showed that carbon dioxide was the *only product* obtained when diamond is burnt in oxygen, and that every 12 parts by weight of diamond yielded 44 parts of carbon dioxide, according to the equation—

$$\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}.$$

Diamond consists, therefore (with the exception of a minute quantity of ash), of pure carbon.

Moissan has recently succeeded in preparing small diamonds artificially from charcoal by means of the electric furnace. Iron and carbon are placed in a crucible which is then introduced into an electric furnace and raised to a high temperature. The iron melts and dissolves the carbon; on now placing the crucible in a bath of molten lead the outer layer of iron solidifies, contracts, and in so doing exerts great pressure on the still liquid metal inside. Under these conditions some of the carbon crystallises out in the form of diamond. The iron is dissolved in hydrochloric acid, and the residue is found to contain small diamonds, some of which are colourless, others are black (called carbonado). A portion of the residue is also in the form of graphite.

(2) *Graphite.*—This also occurs naturally, being found usually in the older crystalline rocks. Cast-iron contains plates of this form of carbon, which can be seen at a freshly-fractured surface, and masses of it accumulate at the base of blast furnaces. It is a soft, dark-grey substance, with an almost metallic lustre, and possesses a much lower specific gravity (2·2) than diamond.

It is usually found massive, but occasionally in six-sided crystals. When rubbed on paper it leaves a black mark, and is therefore used in making lead pencils. It is (unlike diamond) a good conductor of heat and electricity, and on the latter account is used in electrotyping. Graphite is very infusible, and on this account is largely used in the manufacture of "plumbago" crucibles. It is also used as a lubricant for machinery and for polishing gunpowder. When strongly heated in oxygen graphite burns with formation of carbon dioxide; the ash which is left consists of silica, ferric oxide, and alumina. Graphite is oxidised when gently heated with a mixture of $KClO_3$ and HNO_3, whilst diamond is unattacked.

Artificial graphite is now manufactured by heating charcoal or coke with excess of iron in the electric furnace.

(3) *Amorphous carbon* is familiar to us as charcoal, lamp-black, or animal charcoal, which, however, are usually more or less impure forms of carbon.

266. **Charcoal** may be obtained by strongly heating wood or many other organic bodies in vessels from which air is excluded; or by the action of dehydrating substances, such as strong sulphuric acid, on these bodies.

Exp. 160.—Heat a few pieces of wood in a hard glass tube over the flame of a Bunsen burner. Volatile vapours are at first given off and burn at the mouth of the tube; when these are no longer to be seen, throw out the contents of the tube into water. The black charred product is wood charcoal.

Exp. 161.—Make about 100 grammes of sugar into a thick syrup by dissolving it in a small quantity of hot water, and place it in a deep glass cylinder; then pour in about 100 c.c. of concentrated sulphuric acid. Presently the liquid will blacken and froth considerably, and a mass of black charcoal much more bulky than the sugar originally taken will be formed. Wash this thoroughly with water till free from acid, and there remains carbon in a granular condition.

Where wood is scarce, charcoal is prepared from it by distillation, as already mentioned; but where it is plentiful and waste is not important, the logs are arranged in heaps, covered with sods or earth to allow only a small supply of air, and then slowly burned.

267. **Properties of Charcoal.**—The chemical composition and properties of charcoal vary considerably with the kind of wood used and the temperature at which it is charred. When charred at a low temperature the charcoal is soft and light in colour, and it burns easily; it also contains a lower percentage of carbon than when charred at a high temperature. Thus a specimen of wood charred at a temperature of about 300° C. contained 70 per cent. of carbon and 4·5 per cent. of hydrogen, while when charred at a full white heat it contained 96 per cent. of carbon and 0·5 per cent. of hydrogen.

Wood charcoal has a specific gravity of about 1·5; yet when dry it floats on water. This is explained when a piece of charcoal is placed on water under the receiver of an air pump: as the pump is worked, air escapes from the charcoal and it gradually sinks. The charcoal is porous, and the air contained in its pores reduces its apparent specific gravity to about 0·2, the specific gravity of air being only about 0·0013 (water = 1).

Charcoal also absorbs other gases to a varying extent.

Cocoa-nut charcoal, under favourable conditions, was found to absorb of—

Ammonia	172	times its volume.
Hydrochloric acid ...	165	,, ,, ,,
Nitrous oxide ...	99	,, ,, ,,
Carbon dioxide ...	97	,, ,, ,,

On the other hand, charcoal only absorbs slightly more than its own volume of hydrogen.

Exp. 162.—Fill a test-tube with dry ammonia gas by displacement, and stand it over mercury in a trough. Heat a small piece of charcoal red hot in the crucible tongs, and plunge it, while still glowing, under the mercury; then allow it to rise into the test-tube. The mercury rises in the tube as the ammonia is rapidly absorbed by the charcoal.

This property of charcoal is used in deodorising and disinfecting sewers and hospital wards. The charcoal not only absorbs gases and the effluvia evolved by putrefying matter, but also rapidly oxidises them by means of the oxygen already present in its pores: this oxygen is more active than ordinary gaseous oxygen, and is even capable of killing bacteria.

Exp. 163.—Mix a little finely-powdered wood charcoal with water, and pour the whole on to a filter paper in a funnel. Pour some sulphuretted hydrogen water through the charcoal and test the filtrate by lead acetate solution. No black precipitate of lead sulphide is formed, showing that the sulphuretted hydrogen has been oxidised by the oxygen absorbed in the charcoal.

Charcoal also possesses the power of decolorising liquids; for this purpose animal charcoal is more generally used (see § 270).

Charcoal burns in air without flame or smoke, unless it has been prepared at a low temperature and is therefore very impure; in excess of air carbon dioxide (CO_2) is produced, but in a limited supply of air carbon-monoxide (CO) is formed.

268. **Reducing action of Charcoal.**—On account of the ease with which it combines with oxygen, charcoal (and other forms of amorphous carbon) acts as a strong reducing agent at high temperatures.

We have already had an example of a *gaseous* reducing agent in hydrogen, which, owing to its affinity for oxygen, reduces many oxides to the metallic condition. Also in sulphurous acid or phosphorous acid we have instances of *liquids* as reducing agents, their activity being due to the ease with which they undergo oxidation to sulphuric acid and phosphoric acid respectively. In carbon we have a *solid* reducing agent which finds very frequent employment in operations conducted at high temperatures, the carbon under such conditions being oxidised to carbon monoxide or dioxide at the expense of the oxygen contained in the bodies with which it is mixed.

Thus, most metallurgical operations involving a reduction of oxides to the metal are carried out with the use of carbon in the form of coke or coal, which is oxidised to CO or CO_2 in the process.

Exp. 164.—Make an intimate mixture of about a gramme of finely-powdered oxide of lead (litharge) with about one-tenth its weight of charcoal, and heat to redness in a hard glass tube or porcelain crucible for five minutes. Now throw some of the powder into a mortar with a little water and rub it up, using pressure, with the pestle, and then wash away the charcoal by means of a stream of water. Pellets or plates of metallic lead will be obtained—

$$2\,PbO + C = 2\,Pb + CO_2.$$

Similarly, oxide of copper or bismuth may be reduced, and metallic copper or bismuth obtained from them. The reduction of iron ores, or oxide of zinc or tin, are examples of similar reductions carried out on the large scale.

269. Preparation of pure Charcoal.—*Pure* charcoal may be prepared by dehydrating pure cane-sugar as in Exp. 161, and then heating it in a current of chlorine, when any hydrogen present is removed as hydrochloric acid. An alternative method is to heat the cane-sugar in a platinum crucible when water is driven off; the product is then treated with chlorine as before.

270. Animal Charcoal, or Bone Black.—Another kind of charcoal is made by heating bones in closed iron retorts. It is a very porous mixture of charcoal with the mineral constituents of the bones, chiefly calcium phosphate. It is used for decolorising raw sugar, as it has the property already referred to of removing many colouring matters from solution.

Exp. 165.—Shake up with animal charcoal a hot solution of indigo or litmus for a few moments and then pour it on a filter; the filtrate will be colourless. That the colouring matter is removed by the animal charcoal and not by the filter, may be shown by pouring a similar solution, which has not been treated by animal charcoal, through a filter paper.

271. **Lamp-black** may be made by burning resin or turpentine, and bringing a cool surface, *e.g.* the under-side of a porcelain basin filled with cold water, into the flame. In this form, after treatment with chlorine, a particularly pure and finely-divided form of carbon is prepared.

Lamp-black is used in making paint and printers' ink.

272. **Gas-carbon and Coke.**—Two forms of amorphous carbon are obtained by the destructive distillation* of coal (see §§ 285, 286), namely, *gas-carbon* and *coke*. The former is nearly pure carbon, but the latter contains all the non-volatile products present in the coal. Gas-carbon is very hard and has a specific gravity of 2·35. It is a good conductor of electricity, and is on this account used for making the carbon electrodes of arc lights.

273. In whatever form it occurs, carbon is infusible, but it volatilizes without fusion at the temperature of the electric furnace. It cannot be considered an element of great chemical activity, since at ordinary or moderate temperatures it does not combine directly with any of the elements except fluorine. At high temperatures, however, carbon does unite directly with a considerable number of elements, *e.g.* oxygen, sulphur, hydrogen, nitrogen, iron and aluminium.

274. **Proof that the Allotropic Modifications of Carbon all consist of the Same Element.**—The best proof consists in showing that whichever allotropic modification is used, 12 parts by weight of it on combustion in oxygen yield 44 parts by weight of carbon dioxide. We have already seen in § 265 that Dumas adopted this method in the case of diamond. The experiment may be carried out in the

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* The process of *destructive distillation* consists in distilling a complex substance, such as wood or coal, out of contact with air.

following manner:—A small quantity of any form of carbon (say graphite) is accurately weighed out in a porcelain "boat" C (Fig. 64); this is then introduced into one end of a hard glass tube, the greater part of which is filled with granulated copper oxide. The tube is closed at each end with a one-holed rubber cork through which passes a short glass tube. The end of the tube at which the boat is placed is connected with a supply of dry oxygen, the other end with a series of bulbs containing strong caustic potash solution. These bulbs, together with a calcium chloride tube A (the object of which is explained in § 213, where a similar experiment is described with sulphur), are weighed, before being placed in position. The tube is now heated in a furnace; at first only the burners under the copper oxide are lighted, but when this becomes red-hot the heating is extended to the boat and a slow current of oxygen is passed through the tube. The carbon burns to carbon dioxide, which passes on and is absorbed by the caustic potash. Any carbon monoxide which is at first formed owing to incomplete combustion is converted into carbon dioxide during its passage over the heated copper oxide. When nothing remains in the boat but a trace of ash, and when bubbles of gas cease to be absorbed in the potash bulbs, the latter are disconnected and after cooling are reweighed (together with the calcium chloride tube). The increase in weight gives the weight of carbon dioxide formed. The boat is also allowed to cool and is reweighed. The difference between the final weight of the boat (which includes the weight of the ash) and the weight of the boat + graphite (previously determined) gives the actual weight of graphite burnt (*i.e.* the ash is allowed for).

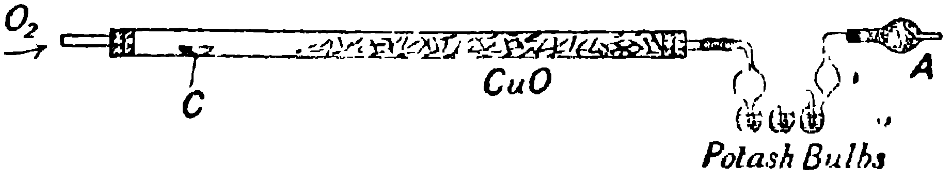

FIG. 64.

Let W_1 = weight of boat + graphite.
W_2 = weight of boat + ash.
Then $W_1 - W_2$ = weight of graphite burnt.
Also let W_3 = weight of KOH bulbs + $CaCl_2$ tube before absorption,
and W_4 = weight of KOH bulbs + $CaCl_2$ tube after absorption,
Then $W_4 - W_3$ = weight of CO_2 formed.

It will then be found that whatever form of carbon is used the ratio $\frac{W_4 - W_3}{W_1 - W_2}$ is equal to $\frac{44}{12}$ or $\frac{11}{3}$.

HYDROCARBONS.

275. These are compounds consisting of carbon and hydrogen alone. The direct combination of carbon and hydrogen in the laboratory can only be effected with difficulty (marsh gas, CH_4, and acetylene, C_2H_2, being formed), and yet the number of known hydrocarbons is exceedingly great

They vary in physical and chemical character according to their composition, and according to the arrangement of the ultimate particles of carbon and hydrogen of which they are composed. Hydrocarbons containing a small number of atoms of carbon and hydrogen are usually gaseous, such as marsh gas, CH_4, ethylene or olefiant gas, C_2H_4, acetylene, C_2H_2; and those whose composition is more complex are at ordinary temperatures liquid, such as pentane, C_5H_{12}, benzene, C_6H_6, oil of turpentine, $C_{10}H_{16}$; or solid, such as naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$.

The hydrocarbons may be arranged in series in accordance with the relative numbers of atoms of carbon and hydrogen which they contain—

(1) The *Marsh Gas Series* (or Paraffins), the first member of which is marsh gas, CH_4, and succeeding members, C_2H_6, C_3H_8, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n+2}.

(2) The *Ethylene Series* (or Olefines), the first member of which is ethylene, C_2H_4, and succeeding members, C_3H_6, C_4H_8, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n}.

(3) The *Acetylene Series*, the first member of which is acetylene, C_2H_2, and succeeding members, C_3H_4, C_4H_6, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n-2}.

(4) Hydrocarbons having the general formula C_nH_{2n-4} and C_nH_{2n-6}, and others having still smaller proportions of hydrogen, are known, a familiar example of the C_nH_{2n-6} series being benzene, C_6H_6, the first member of this series.

At this stage we shall only take into consideration the three hydrocarbons, marsh gas, ethylene, and acetylene.

MARSH GAS OR METHANE, CH_4

276. **Occurrence.**—This gas is so called because it is frequently generated in marshes or pools where vegetable matter is in course of decay. The "blowers" in coal-mines discharge large quantities of this gas, which from its inflammable nature is termed "fire-damp," and it is also formed in the destructive distillation of wood or coal, coal gas containing usually about 35 per cent. of marsh gas.

277. **Preparation.**—When charcoal is heated in an atmosphere of hydrogen to a temperature of 1,200° C. a certain amount of chemical combination takes place, with formation of marsh gas.

It is also produced, together with acetylene, when electric sparks are passed between carbon poles in an atmosphere of hydrogen.

Marsh gas is prepared by strongly heating a mixture of anhydrous sodium acetate and dry soda-lime (lime which has been slaked by the addition of caustic soda solution)—

$$\underset{\text{Sodium acetate.}}{CH_3 \cdot CO_2Na} + NaOH = Na_2CO_3 + CH_4.$$

Exp. 166.—Weigh out about 10 grammes of anhydrous sodium acetate and 30 grammes of soda-lime; intimately mix them in a mortar and dry by gently heating in a porcelain dish. Introduce the mixture into a small hard glass flask provided with a cork and delivery tube, and heat strongly. Collect the gas which is evolved over water at the pneumatic trough.

As thus prepared marsh gas is by no means pure; it is contaminated with ethylene, C_2H_4, and hydrogen. The former may be removed to a large extent by passing the gas through a wash-bottle containing strong sulphuric acid.

Pure marsh gas may be obtained by the action of nascent hydrogen on methyl iodide, CH_3I.

$$CH_3I + \underset{\text{Nascent.}}{2\,H} = CH_4 + HI.$$

The methyl iodide is dissolved in a mixture of alcohol and water and zinc-copper couple added. The two last react with formation of hydrogen which then reduces the methyl iodide. The presence of alcohol is necessary because methyl iodide is insoluble in pure water.

278. **Properties.**—Marsh gas or methane is a colourless and odourless gas, which at 0° C. is condensed to the liquid form under a pressure of 140 atmospheres. It is only slightly soluble in water, 100 volumes of which at 0° C. dissolve 5·5 volumes of the gas. It burns with a pale blue non-luminous flame, forming carbon dioxide and water vapour—

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$

With oxygen or air within certain limits it forms an explosive mixture, and the explosions occurring in coal-mines are usually due to the firing of such a mixture. With the halogen elements * it forms compounds in which part or even the whole of the hydrogen is replaced atom for atom by these elements; this process is known as *substitution*, and the compounds produced are called *substitution products* as already mentioned in § 134. Thus when equal volumes of chlorine and marsh gas are mixed in *diffused daylight*, they gradually react with formation of methyl chloride, CH_3Cl, and hydrochloric acid—

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* *Iodine* does not act directly on marsh gas except in the presence of a substance such as iodic acid, which destroys the HI as soon as it is formed, and so prevents it from exercising a reducing action on the substitution product formed, with re-formation of CH_4.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

If more chlorine is present it gradually replaces the remaining hydrogen till finally the whole of the hydrogen is removed. The equations expressing the reactions which take place are as follows—

$$CH_3Cl + Cl_2 = \underset{\text{Methylene chloride.}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{Chloroform.}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \underset{\text{Carbon tetrachloride.}}{CCl_4} + HCl.$$

On mixing chlorine and marsh gas in direct sunlight an explosion occurs with separation of carbon—

$$CH_4 + 2\ Cl_2 = C + 4\ HCl.$$

279. **Composition of Marsh Gas.**—This may be determined by exploding a known volume (say 30 c.c.) with an excess of oxygen (120 c.c.) in a eudiometer; the carbon and hydrogen unite with oxygen to form carbon dioxide and water vapour respectively. No diminution in volume will occur if the experiment be performed at 100° C., that is, so long as the water remains in the form of vapour; but when the water condenses, a diminution of 60 c.c. will be recorded. Carbon dioxide and the excess of oxygen remain, and the amount of the former may be found by absorbing it with caustic potash; this will give a reduction of 30 c.c., the oxygen excess being 60 c.c. Expressing this shortly we have—

2 vols. marsh gas + 8 vols. oxygen = 4 vols. water vapour + 2 vols. carbon dioxide + 4 vols. oxygen

Now water vapour contains its own volume of hydrogen, and two volumes of marsh gas therefore consist of four volumes of hydrogen, and that amount of carbon which is contained in two volumes of carbon dioxide, *i. e.* one atom. This would give us the composition CH_4.

We find, by weighing, that the density of marsh gas as compared with hydrogen is 8, so that its molecular weight must be 16: this agrees with the formula CH_4, for $C = 12$, H_4 4×1, and $12 + 4 = 16$.

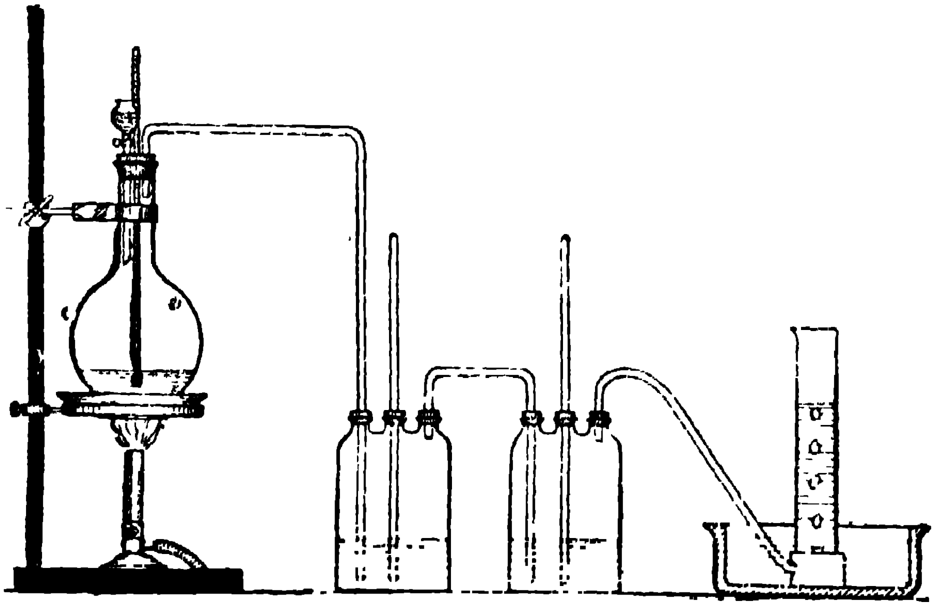


Fig. 65.

ETHYLENE OR OLEFIANT GAS, C_2H_4.

280. This gas occurs as one of the products of the destructive distillation of coal, and the luminosity of the coal gas flame is largely owing to its presence.

Preparation.—Ethylene is prepared by heating a mixture of alcohol, C_2H_5OH, and excess of sulphuric acid. Alcohol behaves towards sulphuric acid just like caustic potash does, *i. e.* it forms a salt with elimination of water—

$$K \cdot OH + H_2SO_4 = KHSO_4 + H_2O.$$
$$C_2H_5 \cdot OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5 \cdot HSO_4} + H_2O.$$

The group of elements C_2H_5 is called ethyl, and plays the part of a metal.

When ethyl hydrogen sulphate is heated, however, it decomposes with formation of ethylene and sulphuric acid—

$$C_2H_5 \cdot HSO_4 = C_2H_4 + H_2SO_4.$$

The last two equations represent, therefore, the two stages of the reaction which takes place in the preparation of ethylene.

Exp. 167.—Mix together 200 c.c. of sulphuric acid and 50 c.c. of water, and cautiously add 50 c.c. of alcohol. Pour into a wide-mouthed flask of about a litre capacity, fitted with a cork through which pass (1) a rather wide delivery tube, (2) a thermometer, (3) a tap funnel (see Fig. 65). Heat the liquid on a sand-bath until the temperature rises to 165° C. and keep as near this as possible. If the alcohol is impure a good deal of frothing occurs, which is, however, less troublesome if sand has been introduced into the flask. The gas should be passed through wash-bottles containing a solution of caustic soda to absorb carbon dioxide and sulphur dioxide, and collected over water, but the first three or four cylinders of it should be rejected, as they contain a very explosive mixture of ethylene and the air displaced from the flask and wash-bottles.

Syrupy phosphoric acid of such a concentration that it boils at 200° C. may with advantage be substituted for sulphuric acid. When this is used the frothing and charring are avoided, and, CO_2 and SO_2 being absent, the washing of the gas may be dispensed with.

281. **Properties.**—Ethylene is a colourless gas which is freely soluble in alcohol, but only slightly soluble in water, 100 volumes of water dissolving about 25·6 volumes of the gas at 0° C. It is more easily condensed to the liquid form than marsh gas, requiring a pressure of

43 atmospheres at 0° C.; the liquid boils at −103° C. under normal pressure. The gas burns with a luminous flame, which is smoky unless it is diluted with hydrogen or marsh gas. It combines directly with chlorine to form an oily liquid, $C_2H_4Cl_2$; hence the name *olefiant* gas.

One molecule of ethylene also combines directly with one molecule of each of the following—bromine, iodine, hydrobromic acid, hydriodic acid, sulphuric acid, and with two atoms of nascent hydrogen. On account of this property of forming *addition* compounds ethylene is said to be *unsaturated;* marsh gas, which only forms *substitution* compounds, is said to be *saturated.*

With oxygen ethylene explodes on ignition much more powerfully than marsh gas, and great care must be exercised in dealing with mixtures of ethylene with air or oxygen.

The composition of ethylene is established by a similar method to that employed in the case of marsh gas.

ACETYLENE, C_2H_2.

282. This gas occurs in small quantity in coal gas, and is formed when coal gas is burnt with an insufficient supply of air, or when the flame is cooled by impinging on a cold surface. Carbon and hydrogen unite directly to form acetylene when a powerful electric discharge is passed between carbon poles in an atmosphere of hydrogen.

Preparation.—One method of preparation is described in the following experiment—

Exp. 168.—Fit into an ordinary lamp-chimney a cork through which passes a short piece of straight wide tubing, and a second narrow piece bent at right angles, as shown in Fig. 66, and connected with the supply of coal gas. Close the aperture at the top of the chimney, and allow the gas to escape by the straight tube until the air is displaced; then light it at the lower extremity of this tube and uncover the aperture at the top of the chimney. The flame will then pass up the tube and attach itself to the inner opening where the air and coal gas meet, the flame area being air and the surrounding atmosphere being coal gas. The gas escaping at the top of the chimney may be ignited, and here we shall have a flame of coal gas burning in air as in combustion under ordinary circumstances. In the flame burning in coal gas at the base of the chimney much acetylene is formed, and if a glass tube be passed through the upper flame and gas be aspirated from the inside of the lamp glass it will be found to contain acetylene. An ammoniacal solution of cuprous chloride absorbs acetylene with the formation of a brown powder, cuprous acetylide, Cu_2C_2, a body which in the dry condition detonates violently by friction or if heated. If this body be prepared by aspirating the gas as above through such a solution, then pure acetylene may be liberated from the moist cuprous acetylide by acting on it with hydrochloric acid—

$$Cu_2C_2 + 2\,HCl = Cu_2Cl_2 + C_2H_2.$$

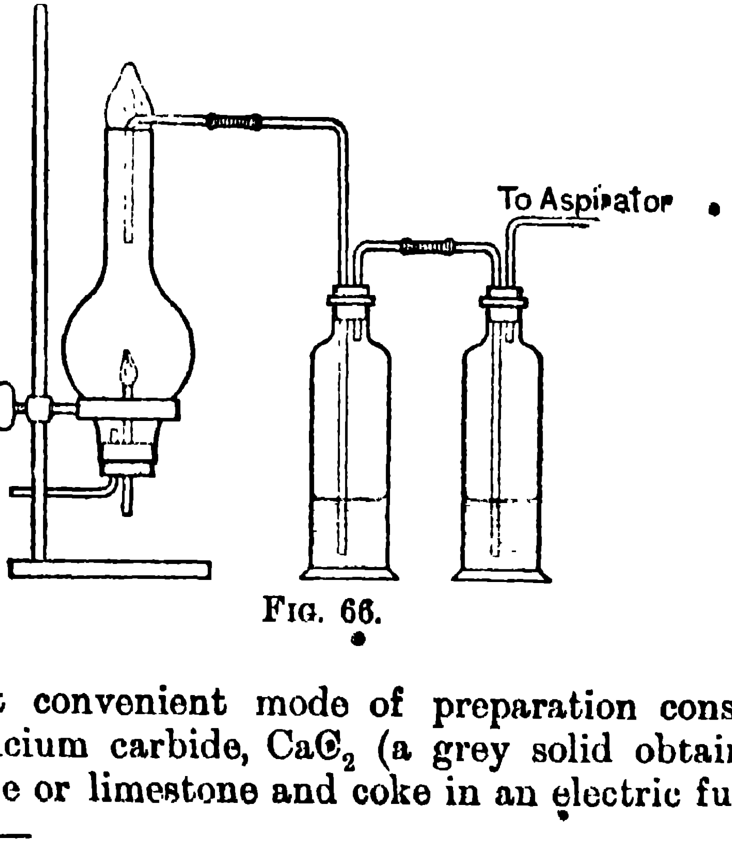


FIG. 66.

The most convenient mode of preparation consists in treating calcium carbide, CaC_2 (a grey solid obtained by heating lime or limestone and coke in an electric furnace), with water—

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$

Exp. 169.—Place a small lump of calcium carbide under a cylinder of water inverted in a trough of water. Acetylene is formed without heating and rises up into the cylinder.

283. Properties.—Acetylene is a colourless gas which possesses an odour of garlic (*not* the odour observed when a Bunsen lamp burns at the base); it is poisonous.

Water dissolves its own volume of the gas at ordinary temperatures, and it may be condensed to a liquid under a pressure of 48 atmospheres. It burns with a luminous smoky flame, and forms very explosive mixtures with air or oxygen.

By using a burner with a very fine hole, the flame of acetylene becomes non-smoky and exceedingly luminous. As might be expected, the gas is employed to a considerable extent for illuminating purposes, *e. g.* in bicycle lamps, and, more recently, for house illumination where coal gas is not available; it is generated as required by the action of water on calcium carbide, for it cannot safely be stored under pressure on account of its tendency to explode when compressed. Acetylene is also used to increase the luminosity of other gases, such as oil gas.

Acetylene combines *directly* with either *one* or *two* molecules of chlorine or bromine; it is therefore more unsaturated than ethylene, which can only take up *one* molecule of each of these elements. It also combines directly with the halogen acids and with nascent hydrogen.

COAL GAS AND WOOD GAS.

284. Before dealing with the manufacture of coal gas on the large scale it will be well to examine the action of heat on coal by experiment.

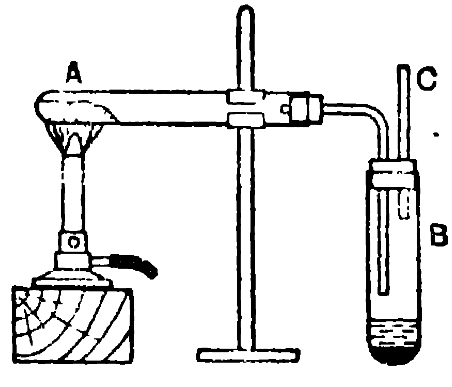
Action of Heat on Coal.—

Exp. 170.—Examine a coal fire, or heat a small piece of coal in a gas flame. You will notice the softening of the coal where it is heated, the giving off of an inflammable gas, and the final burning of the coal. The coal also lights easily.

Exp. 171.—Take a jar of oxygen and lower into it a small piece of coal on a deflagrating spoon after lighting a corner. When the coal has stopped burning, test the contents of the jar for water by means of anhydrous copper sulphate and for carbon dioxide by lime water.

The products of combustion are thus seen to be carbon dioxide and steam.

Exp. 172.--Set up the apparatus shown in Fig. 67. A is a hard glass tube about 6 inches long. B is a wide test-tube. Before placing A in position half-fill it with dry coal dust and shake to make an air space over the coal dust. Heat the tube carefully. Note the formation of smoke and brown fumes which condense to a liquid in B. This liquid separates out into two layers; the upper layer is an aqueous solution of various substances—*gas liquor*, the thick brown lower layer is *tar*. After some time apply a light to the gas escaping at C; it burns: this inflammable gas is *coal gas*. Test the gas with lead acetate paper; note the blackening, showing the presence of *sulphur* compounds in the gas. When the gas has stopped coming off break the tube A and note the hard *coke*.



FIG

285. Manufacture of Coal Gas.—This experiment is repeated on the large scale in the manufacture of coal gas. This process requires the use of special plant, which may be described in outline as follows.

The coal is heated in horizontal tubular fireclay *retorts*, *a*, somewhat ⌓ shaped in section and six or more feet long. The open end of the retort is tightly attached to the iron furnace front *b*, which has for each retort a door *c*, through which coal can be shovelled in and coke removed, and also a vertical iron pipe, the *rising main d*, through which the gas is driven by the decomposition.

The retorts are generally arranged in groups of five for convenience of heating by a single furnace below each group, and are now generally tubular, with a door and rising main at each end.

In order to prevent the escape of gas during the charging of the retorts with coal, a curved pipe leads from the side of the rising main into a horizontal pipe, the *hydraulic main e*. This main contains condensed coal tar and water, below which the entering pipes dip, thus effectually sealing themselves against small changes of pressure. The level of the liquid in this main is kept constant by allowing any excess to flow off into the *tar pit f*.

The gas given off contains vapour of the tar and ammonia, and is too hot to be purified. It is now passed through a series of pipes, the *condensers g*, at first of large diameter to condense the tar, and later of smaller diameter to cool the gas for complete purification and to remove more tar. All the condensed liquids are collected in the tar pit, and separate into two layers, the lower the gas tar, and the upper an aqueous solution containing ammonia and ammonium salts, the *gas liquor*.

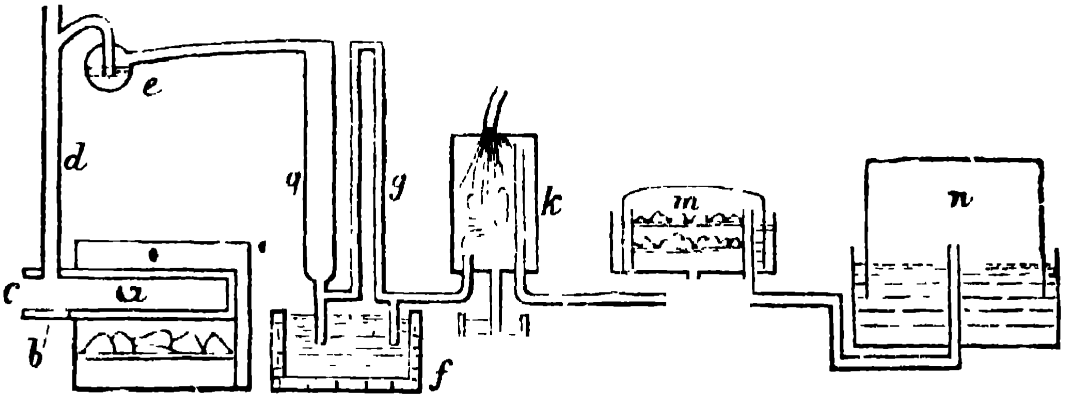


FIG. 68.

From the condensers the gas rises through a larger vessel full of coke, the *scrubber k*, in which it meets a fine spray of water, which removes all traces of ammonia. This liquid, together with the gas liquor from the tar pit, is mixed with sulphuric acid to expel gaseous compounds of sulphur (H_2S, etc.) and to recover the ammonia in the form of ammonium sulphate.

After leaving the scrubber the gas passes through three to six feet of slaked lime contained in the *purifiers m*. These are square gas-tight iron tanks sealed with water, and containing the slaked lime spread on wooden grids in layers about six inches deep. The gas passes through this lime, which absorbs sulphuretted hydrogen and carbon dioxide, and other sulphur compounds, forming a mixture of calcium sulphide, carbonate, etc., the *spent lime* or *gas* *lime.* To remove as much as possible of the sulphur compounds, the gas is generally passed through ferric hydroxide contained in another purifier; the ferric hydroxide is reduced to ferrous sulphide and sulphur is deposited. This mixture on being exposed to the air becomes oxidised, and may be used again until the sulphur is present in too great excess.

After leaving the purifiers the gas passes over into the *gas holders n*, where it is stored over water until it is required for use.

A ton of coal yields about 10,000 cubic feet of coal gas, which varies in composition, but contains approximately—

Hydrogen	50 per cent.
Marsh gas	35 „
Carbon monoxide	8 „
Ethylene, etc....	5 „
Nitrogen and oxygen...	3 „

Thus about 96 per cent. of the product has little or no illuminating power, this property being mostly due to the 5 per cent. of ethylene, etc.

Coal tar is a mixture of many organic substances which are separated by fractional distillation. Among the most important are benzene, naphthalene, anthracene, used in the manufacture of dyes, and phenol (carbolic acid).

286. **Coke.**—The residue in the retorts after the distillation of all the volatile products from coal is composed of two substances, *coke* and *gas-carbon*. The former is found in the centre of the retorts and consists principally of carbon, but contains all the non-volatile mineral matter present in the coal (*i. e.* the ash), and also small quantities of hydrogen, nitrogen and oxygen; the latter occurs as a deposit on the roof and sides of the retorts and is nearly pure carbon. Gas-carbon has been sufficiently fully treated in § 272. We shall, however, study coke at somewhat greater length.

The amount of ash in coke varies with the coal used, but the average composition is—

Carbon	91·5 per cent.
Hydrogen	0·4 „
Nitrogen and oxygen	2·1 „
Ash	6·0 „

Exp. 173.—Try to light a piece of coke in a flame: it does not burn so readily as coal, and requires a higher temperature to set it on fire.

The temperature obtained by burning coke is very high, and, as there are no volatile products, there is generally neither luminous flame nor smoke from dry coke.

Blue flames are often noticed playing above a brightly burning coke fire: these are flames of carbon monoxide, formed by the reaction between carbon dioxide and red-hot carbon.

Coke is not only obtained as a by-product in the manufacture of coal gas, but it is also specially manufactured by heating coal to redness in coke ovens. The coke so prepared is very dense and is used in iron-smelting.

287. **Action of Heat on Wood.**—When wood is heated in the air it chars, gives off inflammable gases, and burns, leaving a black mass of charcoal, which slowly burns away.

Exp. 174.—Repeat Exp. 172, using small pieces of wood (*e. g.* matchstalks) instead of coal dust. Note the formation of water, tar, inflammable gas and charcoal.

Thus the distillation of wood and of coal in absence of air gives similar products; for we obtain wood gas, a water distillate, wood tar, and charcoal. *Wood gas* is used for illuminating purposes in Germany and Switzerland. The temperature of distillation must be very high, however, or the gas does not contain sufficient illuminating gases (heavy hydrocarbons) to be of any use for lighting purposes. The high temperature decomposes a large quantity of liquid oils which would simply distil over if a lower temperature were used. This decomposition is helped by the use of cast-iron retorts instead of clay retorts.

The composition of wood gas as used for illuminating purposes varies between the following wide limits:—

Hydrogen	18 to 42 per cent.
Marsh gas	9 to 35 ,,
Carbon monoxide	23 to 62 ,,
Ethylene, etc....	9 to 35 ,,

Practically no sulphur compounds are produced, but a considerable amount of carbon dioxide is given off, which is removed by slaked lime as in the case of coal gas.

The watery distillate contains only a small quantity of ammonia, but a number of organic substances are prepared from it, of which the chief are wood vinegar (acetic acid), wood spirit (methyl alcohol), and acetone.

Wood tar contains many organic substances, of which creosote is the most important; the latter is used for the preservation of timber.

The residue left in the retort after the distillation is *wood charcoal*, which has already been described.

288. **Mineral Oils.**—Reference has already been made to the naturally occurring mixture of hydrocarbons known as *petroleum* or *natural oil*. The constituents of this mixture have different boiling-points and may, therefore, be separated by distillation, the receiver being changed at intervals. The chief products are:—*Petroleum ether* (b. pt. 40°—70°), *gasoline* and *petrol* (b. pt. 70°—90°)· these three fractions have a specific gravity 0·65—0·70; they are too inflammable for use as illuminants, but are employed as solvents for resins and oils in the manufacture of lacquers and varnishes and for the production of explosive mixtures in gas engines: *benzine* or *benzoline* (b. pt. 90°—120°; sp. gr. 0·70—0·74) is used for dissolving oils and greases and for small lamps; this fraction is also called *ligroin*: *cleaning oil* (b. pt. 120°—170°) is used for the purpose which its name implies, and also instead

of turpentine in making varnishes: *kerosene* or *paraffin oil* (b. pt. 150°—300°) is used for illuminating and heating purposes. The portion which distils over above 300° C. is partly liquid and partly solid at ordinary temperature. The liquid part is called *lubricating oil* and is used for lubrication. The solid is *paraffin wax.* It is separated from any adhering liquid by means of filter presses, and used in the manufacture of candles, night-lights, etc.

Vaseline is the residue which remains when some of the American petroleums are distilled *in vacuo* at low temperatures.

The oils obtained by distillation are generally free from sulphur, but are dark in colour. They are refined by agitation with sulphuric acid, followed by treatment with dilute caustic soda solution, by which means they are rendered nearly colourless and fit for use in lamps.

Shale oil is obtained by distilling *oil shale,* a bituminous shale found in large quantities in the coal measures in Mid-Lothian.' The shale is broken up into small fragments and heated in vertical retorts, and the products of the distillation are passed through a condensing apparatus consisting of a long series of pipes, the arrangement being similar to that used in the manufacture of coal gas, the distillation is assisted by passing steam in at the base of the retorts. The liquid products collect in two layers, the lower consisting of an aqueous solution of ammonia and other substances, and the upper of oil and tar. The latter is a greenish brown mixture closely resembling petroleum, and on fractional distillation it yields a number of products which are very similar to those obtained from petroleum.

289. **Natural Gas.**—In certain localities, particularly Pennsylvania in the United States, a natural gas which consists largely of hydrocarbons has accumulated in cavities in the earth's crust, and when borings are made which reach to these cavities, the gas, which is under great pressure, rapidly rises to the surface. This gas is largely used for illuminating purposes.

Oil gas is made by introducing that portion of shale oil which has a specific gravity of about 0·85 into retorts heated to bright redness, when the complex hydrocarbons of which the oil is composed are broken up, yielding a number of simpler gaseous hydrocarbons. Oil gas is much used for illuminating trains and for enriching coal gas.

QUESTIONS.—CHAPTER XXI.

1. Show in tabular form the percentage of carbon and hydrogen in (*a*) wood, (*b*) peat, (*c*) lignite, (*d*) bituminous coal, (*e*) anthracite.
2. Taking the atmospheric pressure as 15 lbs. on the square inch, calculate the weight of carbon in a column of the air whose base is a square mile, the carbon dioxide present being 0·06 per cent. by weight.
3. Compare the densities of diamond, graphite and amorphous carbon. What do you regard as a full and sufficient proof that each of these bodies consists of the same element?
4. Describe how Moissan has succeeded in preparing artificial diamonds.
5. How would you prove that sugar contains carbon?
6. How is wood charcoal manufactured? Describe experiments illustrating its chief properties.
7. What is animal charcoal, how is it prepared, and for what purpose is it used?
8. How would you show by experiment that a hydrocarbon contains carbon and hydrogen, and that it consists entirely of these elements?
9. Where is marsh gas found to occur naturally, and how is it usually prepared in the laboratory?

10. How can it be proved that the formula for marsh gas is CH_4?
11. Describe in detail the preparation of ethylene from alcohol.
12. Explain the terms—*substitution compound*, *addition compound*, *unsaturated compound*, *saturated compound*.
13. How may marsh gas be distinguished from ethylene?
14. Describe with equations the chemical changes which take place when ethylene is burnt in air and in chlorine.
15. Under what circumstances is acetylene formed during combustion of hydrocarbons? Can you suggest any means of determining the amount of acetylene in a mixture of hydrogen and acetylene?
16. How may acetylene be obtained in the pure condition?
17. What are the chief properties of acetylene, and for what purposes is it employed?
18. Describe how you would investigate experimentally the action of heat on coal in the absence of air.
19. Write a short account of the chief products of the destructive distillation of coal.
20. What are the chief products obtained from crude petroleum, and for what purposes are they employed?
21. State what you know about *natural gas* and *oil gas*.
22. 0·1931 grammes of diamond gave on complete combustion 0·704 grammes of carbon dioxide. Calculate the percentage of ash in the diamond ($C = 12$, $O = 16$).
23. What volume of ammonia will be absorbed by 10 grammes of charcoal if the density of the charcoal is 1·5 and if it absorbs 172 times its volume of the gas?
24. 20 c.cs. of marsh gas are exploded with 50 c.cs. of oxygen. What will be the volume of the resulting gas? Also what diminution in volume will take place on treating the resulting gas with excess of caustic potash?

All volumes are supposed to be measured under standard conditions of temperature and pressure.

25. 30 c.cs. of ethylene are exploded with 150 c.cs. of oxygen and the resulting gas treated with excess of caustic soda. What volume of gas will remain and of what will it consist?

All volumes are supposed to be measured at atmospheric temperature and pressure.

26. 10 c.cs. of acetylene measured at 120° C. and 750 m.m. pressure are exploded with 80 c.cs. of oxygen measured at the same temperature and pressure. What will be the volume of the resulting gas if the temperature and pressure suffer no change, and of what will it consist?

CHAPTER XXII.

COMBUSTION.

290. **Incandescence.**—When the temperature of a body is raised to such a degree that it gives out light, it is said to be incandescent, or in a state of *incandescence.*

Exp. 175.—Take pieces of platinum wire, iron wire, magnesium ribbon, black lead, charcoal, and some iron filings. Heat the first five and drop the filings through a flame, holding the burner aslant. In each case light is given out. While the platinum and iron wires and black lead return to the same state on cooling, the magnesium, charcoal and iron filings are changed by oxidation.

Exp. 176.—Heat carefully about two grammes of ammonium bichromate in a porcelain basin, removing the flame as soon as a change takes place. Note that the change from red crystals to green powder is attended by incandescence.

Incandescence may thus be produced either by external heating or by the heat arising from chemical change.

Liquids and gases may also become so hot as to be incandescent, as in the flash seen during the explosion of a mixture of hydrogen and oxygen. The most common example of the incandescence of gases is afforded by flames.

291. **Flame.**—Whenever a gas or vapour is brought into an atmosphere with which it can react chemically, and the heat generated is sufficient to bring about incandescence of the particles, flame is produced. The heat is generated and the incandescence effected in the region where the reaction is carried on, that is, at the surface where contact occurs between the two gases, as is seen when a jar of hydrogen

burns mouth downwards. When we speak of hydrogen and coal gas as being combustible gases, and of air as being a supporter of combustion, we imply that hydrogen and coal gas, when once ignited, burn in air. In ordinary flames this is the case; we have seen, however, in Exp. 168, that a jet of air can be made to burn in an atmosphere of coal gas.

In either case the flame marks the surface of contact between the air and the coal gas, and is the region where the chemical changes take place which transform the hydrogen and carbon of the coal gas into water and carbon dioxide as ultimate products.

Where the gases are intimately mixed and then ignited the burning takes place with great rapidity, and an explosion of a more or less violent nature ensues; but where a regular supply of the combustible product impinges upon the atmosphere in which it burns, a more or less steady flame is the result, the particular form of which is determined by the nature of the jet and the shaping influence of air-currents.

292. **Point of Ignition.**—In any case, before flame can be produced at all, the temperature of the combustible body must first reach a certain limit known as the *point of ignition*. This temperature varies with different bodies: the vapour of carbon bisulphide may be ignited by a glass rod heated only to 150° C., whilst for hydrogen or coal gas a dull red heat (600° C.) is insufficient.

Exp. 177.—Place in small basins or little tin saucers two or three drops of benzoline, a few drops of paraffin, and a small piece of paraffin wax, and apply a light to each. The benzoline burns at once, the paraffin oil must be slightly warmed, while the paraffin wax must be heated over a burner before it will light. In these cases the temperature of ignition is called the *flash point*.

Conversely, a flame is extinguished if its temperature is by any means reduced below the point of ignition of the vapours consumed in it.

Exp. 178.—Hold a piece of wire gauze (about thirty meshes to the inch) horizontally over a Bunsen burner and about an inch above the orifice (Fig. 69). Turn on the gas and light it on the upper side of the gauze. The flame will not be communicated to the stream of gas on the under side of the gauze.

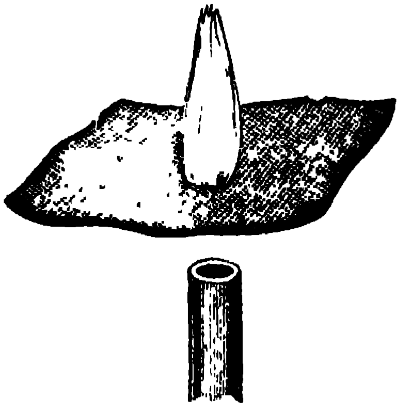


FIG. 69.

This is explained by the fact that the metal of the wire gauze is a good conductor of heat. The heat received from the flame is rapidly conducted away by the gauze and dissipated, chiefly by radiation. This continuous loss of heat prevents the temperature of the gauze from reaching the ignition point of the gas, and, as the gas below the gauze can only become heated by contact with the gauze, it does not become ignited.

Exp. 179.—Make a piece of the wire gauze into a cylindrical roll, and place a candle within it. Now direct the flame of a Bunsen burner against the outer surface of the gauze; the wax may be melted, but the candle cannot be lighted unless the gauze is heated to redness. The reason for this will be gathered from the explanation given in the previous experiment.

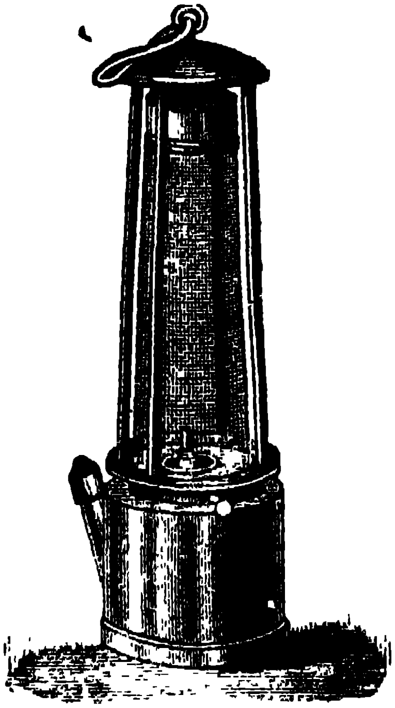


FIG. 70.

The *Davy Lamp* (Fig. 70) is a similar arrangement, in which an oil lamp is shut in by a layer of gauze; and, even if such a lamp be entirely surrounded with inflammable gas, this will not become ignited, although the inflammable gas which passes through the gauze may burn inside it and fill the space above the oil lamp with flame. If, however, the gauze becomes strongly heated, or if the flame should be mechanically driven through the meshes, communication with the inflammable atmosphere outside may be established, and ignition will then take place.

293. The Candle Flame.—The inflammable matter in a candle is the wax or tallow, consisting of compounds containing carbon and hydrogen. The wax is melted and passes up into the wick, which serves as a still supplying the vapours of carbon compounds to the space immediately surrounding it. That such a space exists containing combustible vapours may easily be shown by the following experiment:—

Exp. 180.—Depress a sheet of stout paper quickly into a candle flame to the level of the top of the wick, and hold it steadily there for about a second. On withdrawing it, a ring of sooty deposit will be seen, and within it a clear space. Secondly, take a glass siphon-tube, as shown in Fig. 71, and bring the shorter limb into the centre of the flame; presently yellowish-brown vapours will be seen to pass down the tube and issue at the other end. These vapours will be found to be inflammable, and may be burnt at the end of the tube.

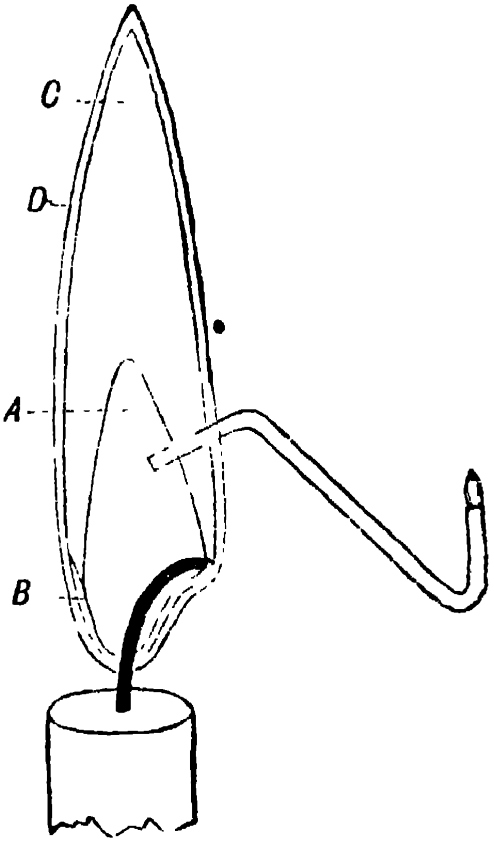


Fig. 71.

We can distinguish in the candle flame—

(1) A central zone surrounding the wick, and containing vapours of carbon compounds—the zone of no combustion (A in Fig. 71);

(2) A blue non-luminous zone, B, at the base;

(3) A luminous zone, C, surrounding the dark central zone; and

(4) A faintly luminous mantle D. Under ordinary circumstances this zone is not easily seen, but if a little finely-powdered common salt is sprinkled over the flame, it will flash out as a golden-yellow fringe, the colour of which is due to the salt.

The mantle can also be seen as a golden band above the wick by looking just above the glowing tip of the wick projecting through the side of the flame.

The changes which take place in the different zones are somewhat as follows:—(A) Vaporisation of the carbon compounds. As these pass up this zone decomposition takes place, with gradual formation of acetylene and from it of dense hydrocarbons, and finally of free carbon particles. (B) The hydrocarbons present undergo partial combustion, with formation of carbon monoxide, hydrogen, and water—

$$CH_4 + O_2 = CO + H_2 + H_2O,$$
$$C_2H_4 + O_2 = 2\ CO + 2\ H_2.$$

(C) The changes which take place in this zone are very complex. The formation of dense hydrocarbons and separation of carbon particles is continued. Also incomplete combustion takes place with formation of carbon monoxide, carbon dioxide, hydrogen, and steam. The luminosity of this zone is due to the presence of the solid carbon particles and dense hydrocarbons, which become incandescent owing to the heat evolved by the chemical reactions which are taking place. (D) Here the products of zones (B) and (C) are mixed with excess of air and burnt completely to carbon dioxide and water.

294. The Gas Flame.—A coal-gas flame has the same four zones as a candle flame unless the jet is very small. As its size is reduced the luminous zone gradually diminishes relatively to the non-luminous zones, and when the jet is very small it entirely disappears. The flame now consists of three zones only, and presents the appearance shown in Fig. 72.

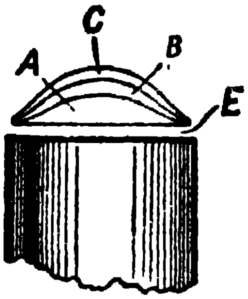


Fig. 72.

A is the zone of no combustion. B is the zone of incomplete combustion; it is blue, like zone B in Fig. 71, to which it corresponds. In the mantle C the combustion is complete. Between the flame and the burner there is a space E containing unburnt gas; it is part of the zone of no combustion.

Exp. 181.—Examine a gas-jet when turned on full, and note the zones as in the candle flame (§ 293). The mantle can be shown to be hot by means of a thin piece of wire held across the flame. Note the changes in the character of the flame as the gas is gradually lowered, and the gradual disappearance of the luminous zone.

295. **Luminosity of Flame.**—There are three factors, some or all of which are concerned in the luminosity of flame—(1) the presence of solid particles; (2) the density of the flame gases; (3) the temperature. At one time it was believed that (1) and (3) were the sole causes; this was Davy's theory, and it was supported by the following facts:—

(*a*) Most flames in which no solid particles can be present are practically non-luminous: *e.g.* hydrogen burning in oxygen.

(*b*) Non-luminous flames become luminous when solid particles are introduced into them: *e.g.* finely-divided charcoal or lime blown into an oxyhydrogen blowpipe flame makes it luminous.

(*c*) A glass rod held in a candle flame becomes covered with soot only on the under side. If the interior of the flame consisted of vapours which deposited soot because they were cooled down by the rod, the deposit should be all round.

(*d*) Luminous flames, like that of a candle, when placed between a brighter light and a screen, cast a shadow; non-luminous flames cast no shadow.

That the luminosity of some flames is not due to the presence of incandescent solid particles is shown by the existence of luminous flames in which no solid matter can possibly be formed: *e.g.* the flame produced when phosphorus or phosphoretted hydrogen burns in oxygen, or arsenic burns in nitric oxide or oxygen. At the temperature of the flame in these cases all the possible products of combustion are gases. According to Frankland's theory, luminosity is due to the presence of heated gases, the luminosity increasing with the density of the gases. This is supported by the following facts:—

(*a*) A candle burns at high altitudes or in an artificially rarefied atmosphere with greatly-reduced luminosity.

(*b*) The flame of hydrogen burning in oxygen becomes luminous when the gases are under a pressure of two atmospheres.

The effect of the temperature of a flame upon its luminosity may be studied by experiment.

Exp. 182.—Make a short coil of stout copper wire by giving it half-a-dozen turns round a piece of glass rod about 5 mm. in diameter, leaving only a small space between one coil and the next. Bring the coil into the upper part of the luminous zone of a candle flame: the flame will become smoky; if it be quickly depressed to the level of the wick, the flame loses its luminosity, and, indeed, may be extinguished altogether.

Exp. 183.—Fill a gas cylinder with oxygen and lower a lighted candle into it: the flame becomes much shorter and brighter.

In the first case, copper, which is a good conductor of heat, conveys away heat from the flame, and lowers its temperature to such an extent that the solid particles of carbon can no longer keep up their luminosity; they escape combustion and pass off as smoke. Indeed, the vapours may also be cooled below their ignition point, in which case the flame is extinguished altogether.

In the second case, the heat given out is not utilised in raising the temperature of the nitrogen of the air, but is all available for heating the particles of carbon.

Thus, raising the temperature of a flame increases its luminosity, and lowering its temperature decreases its luminosity.

The effect of cooling is often noticed in very cold weather, when the gas, if carried by exposed pipes, does not possess its usual illuminating power: this is partly due to the condensation of volatile liquid and solid hydrocarbons contained in the gas, and also to the extra amount of heat required to raise both gas and air to the temperature of incandescence.

In ordinary flames used for various purposes all three causes operate and may be utilised.

296. The Batswing and Fishtail Flames.—In these flames the gas is made to issue from a narrow slit (fishtail) or from two jets which impinge on each other (batswing).

By these devices the flame is flattened. This enlarges the surface of gas exposed to the air, and thus increases the rate of combustion and the luminosity.

297. **The Bunsen Flame.**—This flame is produced by mixing air with the gas which is to be burned, in such quantity as to render the combustion nearly perfect and the flame non-luminous. The gas is supplied through a small jet placed inside a wide tube, so that the rush of gas sucks in air through holes at the bottom; the mixture of gas and air passes up the tube, and is ignited at its mouth.

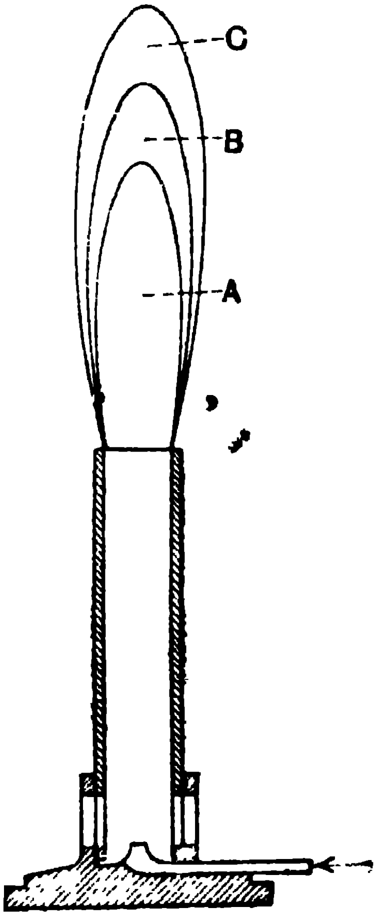


FIG. 73.

The Bunsen flame consists of three zones (Fig. 73). A is the zone of no combustion. In B (pale blue) incomplete combustion takes place, the hydrocarbons being in excess, and in C (very pale blue) the combustion is complete, air being in excess. The non-luminosity of a Bunsen flame is caused by (1) increased oxidation by which the separation of solid particles of carbon is prevented, or at any rate reduced; (2) dilution by the nitrogen of the air—this raises the temperature required for the decomposition of the hydrocarbons of coal gas; (3) cooling by the large volume of air introduced. The result of (2) and (3) is that the gases reach the outer zone where air is in excess and are completely burnt up, before they attain the temperature at which dense hydrocarbons are formed and carbon particles separate.

298. Oxidising and Reducing Flames.—The foregoing paragraphs show that heated hydrocarbon vapours have the power of combining with oxygen in the gaseous condition to form carbon monoxide or dioxide, hydrogen, and water vapour. They have thus the power of abstracting oxygen from many solid oxides or bodies containing oxygen. This property may readily be shown either by means of the flame of a Bunsen burner or of the blowpipe.

Exp. 184.—Partially close the holes at the base of the Bunsen burner until there appears a well-defined luminous tip (A in Fig. 74) within the flame owing to the reduction of the air supply. Now introduce within the luminous area a small amount of barium sulphate on a loop of thin platinum wire, and hold it there steadily for two or three minutes.

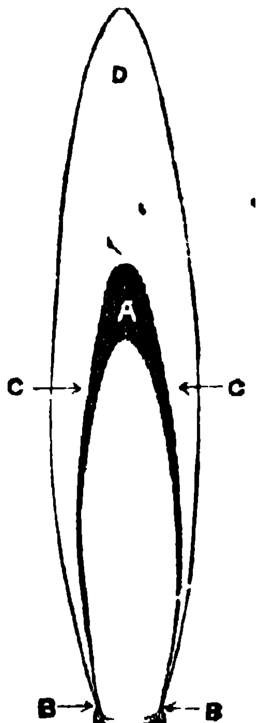


FIG. 74.

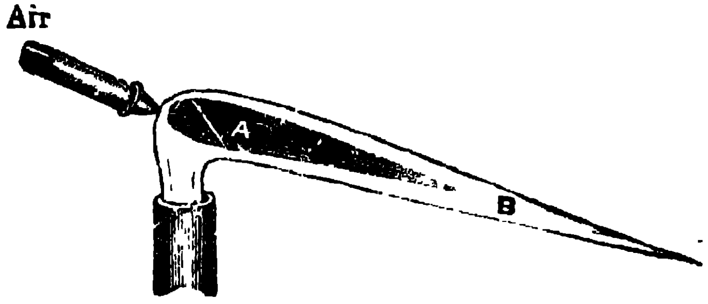


FIG. 75.

In Fig. 74
A is reducing area
BCD is oxidising area
B low temperature oxidising area
C high „ „ „

In Fig. 75
A is reducing area
B is oxidising area

The substance will be found to have changed in character, for, whilst the barium sulphate originally taken is unacted upon by hydrochloric acid, the resulting body when moistened with dilute hydrochloric acid evolves an odour of sulphuretted hydrogen. The sulphate of barium ($BaSO_4$) has been deprived of its oxygen, and has become barium sulphide (BaS); this on treatment with dilute hydrochloric acid is transformed into the soluble chloride of barium with the evolution of sulphuretted hydrogen (H_2S)—

$$BaS + 2\ HCl = BaCl_2 + H_2S.$$

Similarly, oxide of lead or copper may be reduced to metallic lead or copper when brought into the inner flame A of the blowpipe (Fig. 75). Wherever in a flame the hydrocarbons predominate and the supply of oxygen is limited such a *reducing* action prevails; and wherever in a flame the supply of oxygen is in excess of that required to consume the hydrocarbons, as in the outer zone of the candle or the Bunsen burner or the blowpipe flame, an *oxidising* action is experienced. This may be shown by bringing metallic tin or other metals into the outer margin of the Bunsen flame.

299. **Definition of "Combustion."**—The term *combustion* has hitherto been used in the popular sense to indicate the burning of a substance in air. Chemists, however, usually assign a broader meaning to the term, as follows:—*Combustion is chemical reaction between two substances accompanied by the production of heat and light.* There is no restriction as to the nature of the reacting substances. Some writers include under the term combustion such processes of oxidation as the rusting of iron in moist air, in which heat only, not light, is produced; but this is, perhaps, carrying the use of the term too far.

Usually the substance which is *outside* during the combustion is spoken of as a *supporter of combustion*, and that which is *inside* as the *combustible body;* but, as has been shown above in the case of coal gas and air, the supporter of combustion and the combustible body can change places. This holds also in other cases, so that the terms are only relative.

Since the external substance is usually air, a substance is commonly said to be combustible or not according to whether it will or will not burn in air. Thus, hydrogen, phosphorus, and carbon monoxide are combustible; chlorine and nitrous oxide are not combustible.

Again, a substance is said to be a *supporter of combustion* if it will allow the same substances to burn in it as burn in air (*e.g.* coal gas, hydrogen, a taper). Chlorine and nitrous oxide are supporters of combustion; sulphuretted hydrogen, carbon monoxide, and hydrogen are not.

Strictly speaking, however, any two substances which can exist in the gaseous state and which can combine chemically with sufficient evolution of heat may occupy towards each other the positions of supporter of combustion and combustible body interchangeably. For example, a jet of hydrogen will burn in chlorine, and a jet of chlorine will burn in hydrogen. In the former case hydrogen is the combustible body and chlorine the supporter of combustion; in the latter the reverse. Again, phosphorus burns in oxygen; but it would be possible to burn oxygen in phosphorus vapour, in which case the latter would be the supporter of combustion.

300. **Heat of Combustion.**—Whenever carbon, hydrogen, or bodies containing carbon and hydrogen burn, by combining with the oxygen of the air (the carbon to form carbon monoxide or dioxide, and the hydrogen to form water), the amount of heat accompanying the change is perfectly definite and constant.

If a gramme of pure carbon be burnt to carbon dioxide, the heat given out will be sufficient to raise the temperature of 8,080 c.c. of water 1° C.; this is expressed shortly by the statement that the *heat of combustion* of one gramme of carbon is 8,080 thermal units or calories. So, in like manner, the combustion of one gramme of hydrogen is found to give rise to the evolution of 34,200 thermal units. Hydrogen, therefore, on combustion gives out more than four times the amount of heat evolved by the same weight of carbon.

Bituminous coal consists chiefly of carbon, but, as it contains some hydrogen, it should give out more heat on combustion than the same weight of carbon, and it would do so but for the fact that it contains usually 15 to 20 per cent. of oxygen, sulphur, nitrogen, and mineral ash, which are practically unproductive of heat. In anthracite, however, these constituents amount to little more than 5 per cent., and the heat of combustion of this kind of coal is greater than that of bituminous coal.

Petroleum, consisting entirely of carbon and hydrogen, and containing much more hydrogen than coal, actually does give out more heat than the same weight of carbon.

Fuel being employed for heating purposes, the amount of heat generated in its combustion is of primary importance, and the following table shows at a glance the comparative value of different substances which are applicable as fuels :—

Hydrogen ...	34,200	thermal units	per gramme consumed.
Petroleum ...	12,000	,,	,,
Coal ...	7,500 to 8,500	,,	,,
Carbon ...	8,080	,,	,,
Wood ...	about 3,000	,,	,,

QUESTIONS.—CHAPTER XXII

1. Explain the term *incandescence*, and describe experiments which show how it may be produced.
2. What conditions are necessary for the production and continuance of combustion? How would you show them experimentally?
3. Describe an experiment by which air may be made to burn in coal gas.
4. Explain what is meant by *point of ignition* and *flash point*.
5. Explain the principle of the *Davy lamp*, and describe an experiment which illustrates it.
6. Describe the structure of a candle flame, and explain the nature of the chemical changes which take place in the different zones.
7. Describe the appearance of a coal-gas flame which is burning very low.

8. Discuss the explanations which have been put forward to account for the luminosity of flame.
9. Give a diagram of the Bunsen flame, and indicate on it

   (*a*) the reducing area;
   (*b*) the oxidising area;
   (*c*) the high temperature oxidising area;
   (*d*) the low temperature oxidising area.

10. What are the causes of the non-luminosity of a Bunsen flame?
11. How may calcium sulphate be reduced to calcium sulphide
    (*a*) in the blowpipe flame;
    (*b*) in the Bunsen flame?
12. Explain carefully what you understand by *combustion*, and *supporter of combustion.*
13. What volume of water may be raised from 10° C. to 50° C. by the heat derived from the combustion of 10 grammes of hydrogen and 10 grammes of carbon respectively?
14. Explain the term *heat of combustion*, and compare the heats of combustion of the common kinds of fuel.

CHAPTER XXIII.

OXIDES OF CARBON—CARBON BISULPHIDE.

CARBON forms two compounds with oxygen, namely, carbon monoxide, CO, and carbon dioxide, CO_2.

CARBON MONOXIDE, CO.

301. **Occurrence.**—This gas occurs in small quantity in chimney gases, especially where the air-supply during combustion is not in sufficiently large excess ; it is also formed during the dry distillation of wood, coal, and such organic bodies. The gases from blast or other furnaces in which an excess of carbon is present, and in which a reducing operation is being performed, consist largely of carbon monoxide.

302. **Preparation from Oxalic Acid.**—Carbon monoxide may be prepared by heating oxalic acid with concentrated sulphuric acid, an equal volume of carbon dioxide being given off at the same time.

Exp. 185.—Introduce about 20 grammes of crystallised oxalic acid into an 8-ounce flask provided with thistle funnel and delivery tube, and as much concentrated sulphuric acid as to cover it. Apply heat steadily until effervescence sets in, and then moderate it so as to secure a regular and not too rapid evolution of the gas. Collect over water, avoiding any escape of the gas, as it is very poisonous. The reaction which takes place is—

$$C_2H_2O_4 + H_2SO_4 = CO + CO_2 + \underbrace{H_2O + H_2SO_4}.$$

The sulphuric acid removes the elements of water from the oxalic acid without itself undergoing any chemical change.

303. **Experimental study of the products of the reaction**—

Exp. 186.—Pour lime-water into a jar of the gas, and shake up; the lime-water will become turbid owing to the formation of calcium carbonate *—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The presence of carbon dioxide is thus indicated.

Exp. 187.—Remove the cover from a jar of the gas, quickly pour in a few cubic centimetres of caustic soda, replace the cover and shake up well; the carbon dioxide will combine with the caustic soda, forming sodium carbonate—

$$2\,NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Now bring the mouth of the jar under water, and remove the cover; the water will rise, and it will be seen that about half the volume of the gas is left. This is the carbon monoxide. Transfer some of this gas to a smaller vessel by decanting it over water, and shake up with lime-water; no turbidity will be produced, the carbon dioxide having been removed. Now apply a light to the gas; it will burn with a beautiful blue lambent flame. When the combustion is finished, again shake up the vessel, and marked turbidity will then be produced, showing that carbon dioxide has again appeared. The carbon monoxide has united with oxygen during the process of combustion, with the formation of carbon dioxide—

$$2\,CO + O_2 = 2\,CO_2.$$

It may also be noticed that carbon monoxide does not itself support combustion, for if whilst it is burning the lighted taper be plunged into the vessel, the flame will be extinguished.

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* After the experiment has been performed, it is well to burn the gas rather than to let it escape directly into the air.

Exp. 188.—Remove the carbon dioxide from a second jar of the collected gas, and then decant into the jar sufficient air to fill the vessel.

We have now a mixture of equal volumes of carbon monoxide and air, and if after allowing the gases to stand for two or three minutes to mix properly, the mouth of the jar be held towards the flame of a Bunsen burner, it will be seen that carbon monoxide and air form an explosive mixture.

If it be desired to separate the carbon dioxide from the monoxide before collecting the gas this may be done by passing the gases evolved during its preparation through two wash-bottles containing caustic soda solution, as shown in Fig. 65.

304. Other methods of preparation.—Carbon monoxide may, however, be prepared free from the dioxide by gently warming a mixture of sodium formate and sulphuric acid—

$$H\cdot COONa + H_2SO_4 = NaHSO_4 + H_2O + CO.$$

This is the method usually adopted in the laboratory.

Another convenient method of preparation consists in heating roughly-powdered potassium ferrocyanide, $K_4FeC_6N_6 + 3\,H_2O$, with concentrated* sulphuric acid. The change which takes place is represented by the equation—

$$K_4FeC_6N_6 + 6\,H_2SO_4 + 6\,H_2O = 2\,K_2SO_4 + FeSO_4 + 3\,(NH_4)_2SO_4 + 6\,CO.$$

The water required for this reaction is derived partly from the water of crystallisation of the ferrocyanide and partly from the 1·5 per cent. of water present in the sulphuric acid.

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* *Dilute* sulphuric acid gives rise to the formation of hydrocyanic acid (HCN).

An interesting method whereby carbon monoxide may be obtained in large quantities, though in an impure condition, is to pass carbon dioxide over red-hot charcoal. The charcoal may conveniently be heated in an iron pipe by means of a combustion furnace, and the carbon dioxide evolved in a gentle stream by the action of hydrochloric acid on marble—

$$CO_2 + C = 2\ CO.$$

The carbon monoxide is either collected or burnt at a jet attached to the exit of the tube.

This method of formation may be observed in a coke or red-hot cinder fire, on the surface of which the blue flames of the burning gas may be seen. The air passing in at the base of the fire at the lower part of the grate unites with carbon, forming carbon dioxide, and this as it passes over the mass of red-hot carbon in the upper part of the grate is transformed into carbon monoxide. "Producer gas" or "generator gas," used in some manufacturing operations, consists largely of carbon monoxide, and is obtained by passing air over a high column of red-hot coke or anthracite.

When steam is passed over red-hot coke a mixture of carbon monoxide and hydrogen is formed, which is known as *water-gas*—

$$H_2O + C = CO + H_2.$$

Water-gas is used on the large scale as a source of heat.

305. **Properties.**—Carbon monoxide is a colourless, tasteless gas; it is only very slightly soluble in water, 100 volumes of water at ordinary temperatures dissolving less than three volumes of the gas. It is also very difficult to condense, the liquid boiling under atmospheric pressure at $-190°$ C. Under ordinary circumstances, carbon monoxide burns in air, or may be exploded with oxygen in a eudiometer, forming carbon dioxide. But when the gases are *perfectly dried* by exposing them for a lengthened period to phosphorus pentoxide, sparks may be passed

through the mixture without combination taking place. This affords us with yet another example of the influence of moisture in assisting chemical reaction.

Owing to the readiness with which carbon monoxide combines with oxygen, it is a powerful reducing agent at high temperatures. It also combines directly with the vapour of sulphur, forming carbonyl sulphide (COS), and in sunlight with chlorine, forming carbonyl chloride ($COCl_2$), also known as phosgene gas.

Finely-divided nickel and iron unite with carbon monoxide on heating, forming compounds called *carbonyls;* nickel carbonyl is represented by the formula $Ni(CO)_4$ and iron carbonyl by $Fe(CO)_5$; both these compounds are liquids.

Carbon monoxide dissolves in a solution of cuprous chloride in strong hydrochloric acid or ammonia, with formation of a compound $Cu_2Cl_2 \cdot CO$. A solution of cuprous chloride is used as an absorbent for CO in gas analysis.

Carbon monoxide is a very poisonous gas, this property depending on its power of combining with the hæmoglobin of the blood to form a bright red compound, carboxyhæmoglobin.

306. **Composition.**—The composition of carbon monoxide may be ascertained by exploding the gas in a eudiometer along with oxygen. It will be found that 100 volumes of carbon monoxide and 100 volumes of oxygen after explosion show a contraction to 150 volumes, and on absorbing the carbon dioxide formed by means of potash, 50 volumes of oxygen will remain. Thus 100 volumes of carbon monoxide have united with 50 volumes of oxygen to form 100 volumes of carbon dioxide.

This agrees with the formula CO for carbon monoxide assuming the formula for carbon dioxide to be CO_2 (see § 311 for proof of this)—

$$\underset{\text{4 vols.}}{2\,CO} + \underset{\text{2 vols.}}{O_2} = \underset{\text{4 vols.}}{2\,CO_2}.$$

The density of carbon monoxide affords a confirmation of this formula. The gas is fourteen times as heavy as hydrogen, and therefore its molecular weight is 2 × 14 or 28, that of hydrogen being 2.

Now $C = 12$, $O = 16$, and therefore $CO = 12 + 16$ or 28, so that, as already stated, CO is the correct formula for carbon monoxide.

CARBON DIOXIDE (CARBONIC ACID GAS), CO_2.

307. **Occurrence.**—This gas is of more frequent occurrence than carbon monoxide. Its presence in air and water has already been mentioned, and also the part it plays in the animal and vegetable kingdoms. It is given off in large quantities from lime-kilns, in which the limestone ($CaCO_3$) is decomposed by heat into quicklime (CaO) and carbon dioxide. Processes of fermentation and putrefaction give rise to the gas. Whenever an explosion of fire-damp occurs in coal mines carbon dioxide is formed in large quantities, and constitutes what the miners call the *after-damp* or *choke-damp*.

308. **Preparation.**—The usual method of preparing carbon dioxide, namely, by the action of dilute hydrochloric acid on limestone or marble, has already been described in Exp. 57, § 41. The reaction which takes place is represented by the equation—

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

Although somewhat soluble in water, the gas may be collected over water as in Exp. 41, but as it is much heavier than air, it is usually collected by downward displacement. All carbonates, when treated with dilute hydrochloric acid, liberate carbon dioxide; many, such as limestone, liberate it when heated.

We have already seen that carbon dioxide is formed when carbon or compounds containing it are burnt in excess of air. If carbon compounds are heated to redness with oxide of copper, the whole of the carbon is transformed into carbon dioxide, and it is in this way that the amount of carbon in such compounds is estimated.

309. **Properties of Carbon Dioxide.**—These have already been studied by experiment in § 41, Exp. 48. Carbon dioxide is a colourless gas with a faintly acid taste and smell. It is about 1½ times as heavy as air, and its high density may be illustrated by the following experiment:—

Exp. 189.—Fill a large beaker of three or four litres capacity by downward displacement with carbon dioxide; now detach a soap-bubble charged with air into the beaker, and it will be found to float on the surface of the heavier carbon dioxide.

Carbon dioxide is soluble in water, which at 15° C. dissolves about its own volume of the gas, while at 0° C. 100 volumes of water dissolve 180 volumes of the gas. As with other gases, the amount dissolved increases directly as the pressure under which solution takes place, and soda-water being water charged with the gas under about four atmospheres pressure contains about four times its volume of the gas. The aqueous solution of carbon dioxide possesses feebly acid properties, for it is able to change the colour of litmus from blue to *claret* (not to the *bright red* produced by strong acids such as HCl and H_2SO_4); CO_2 can also, like other acids, decolourise phenol-phthalein which has been rendered pink by the addition of a small quantity of alkali.

Exp. 190.—Pass a stream of carbon dioxide through a few cubic centimetres of water to which some drops of litmus solution have been added, and note that the litmus assumes a claret tinge; contrast this with the effect of adding litmus to water containing a little hydrochloric or sulphuric acid. Notice also that by boiling, the carbon dioxide is expelled, and the litmus assumes its original colour. A solution of carbon dioxide in water is therefore very unstable, and possessed of a feebly acid character.

Exp. 191.—Pass the expired air from the lungs, or carbon dioxide prepared from marble and washed free from hydrochloric acid by passing through water, through a slightly alkaline pink solution of phenol-phthalein; the pink liquid becomes colourless.

Carbon dioxide is in general a non-supporter of combustion and of animal life. Certain metals, however, such as magnesium and potassium, will burn in it with liberation of carbon.

$$\begin{aligned} 2\,Mg + CO_2 &= 2\,MgO + C. \\ 4\,K + 3\,CO_2 &= 2\,K_2CO_3 + C. \end{aligned}$$

It is decomposed by the green colouring-matter of plants in presence of sunlight, carbon being assimilated and oxygen set free in the process.

Though the harmful effects of carbon dioxide are mainly due to suffocation (*i.e.* absence of oxygen), yet at the same time the gas does exercise a directly poisonous action on the system ; for air containing more than one volume of it per thousand (*i. e.* about three times the normal quantity) has a distinctly depressing effect, and often gives rise to headache.

310. **Liquid and Solid Carbon Dioxide.**—Under a pressure of 36 atmospheres at 0° C. the gas condenses to the liquid form, and in this form it is prepared on a tolerably large scale and stored in steel cylinders. If the nozzle of one of these cylinders be opened, the pressure being released, the liquid is rapidly transformed into gas. The amount of heat absorbed by the passage from the liquid to the gaseous condition is considerable, and the issuing gas becomes so far cooled that a part of it condenses again even to the solid form. Solid carbon dioxide is a white, snow-like substance which passes only comparatively slowly into the gaseous condition again. The depression of temperature caused by its passage from the solid to the gaseous condition is such that mercury can be readily cooled down to − 40° C. and obtained as a solid body.

311. **Composition of Carbon Dioxide.**—This may be shown by a method similar to that employed in the case of sulphur dioxide. Thus when carbon is burnt in oxygen no change of volume occurs, and carbon dioxide is therefore said to contain its own volume of oxygen. It follows from Avogadro's hypothesis that the formula for the gas may be written C_xO_2 where x has yet to be determined. Now the

molecular weight of carbon dioxide as deduced from its density is 44. This agrees with the value $x = 1$ in the formula just given for $C = 12$, $O = 16$ and $C_1O_2 = 12 + 2 \times 16$ or 44. The formula for carbon dioxide is therefore CO_2.

The composition by weight of the gas agrees with this formula, for, as already stated in § 265, 12 parts by weight of carbon unite with 32 parts of oxygen to produce 44 parts of carbon dioxide.

312. **The Carbonates.**—We have seen in a previous paragraph that a solution of carbon dioxide in water shows a feebly acid reaction. For this reason, and from a consideration of the salts known as the carbonates, carbon dioxide is to be regarded as the anhydride of carbonic acid, and the composition of the acid, although never isolated, may be taken as H_2CO_3.

Carbonic acid has two atoms of hydrogen replaceable by metals, and is therefore a *dibasic* acid. In the acid carbonates or *bicarbonates* only half the hydrogen is so replaced; thus $KHCO_3$ is bicarbonate of potash, and $NaHCO_3$ is bicarbonate of soda. In the normal carbonates the whole of the hydrogen is replaced, as with K_2CO_3, potassium carbonate, and Na_2CO_3, sodium carbonate.

Exp. 192.—Pass carbon dioxide to saturation into a solution of caustic soda, and then evaporate down to dryness on a water-bath. A residue will be obtained consisting of the monohydrated normal carbonate of soda, $Na_2CO_3 \cdot H_2O$.

Dissolve as much as possible of this in hot water and allow to cool; crystals of $Na_2CO_3 \cdot 10\,H_2O$ will be formed. This is the product known as "soda crystals," and used as washing soda.

On very gently warming a quantity of soda crystals, or preferably $Na_2CO_3 \cdot H_2O$, in an atmosphere of carbon dioxide, the salt takes up CO_2 and is transformed into the bicarbonate, $NaHCO_3$—

$$Na_2CO_3 \cdot H_2O + CO_2 = 2\,NaHCO_3.$$

Exp. 193.—Heat in a porcelain basin over the Bunsen flame a few grammes of dry bicarbonate of soda; carbon dioxide will be given off, and the normal carbonate reproduced—

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbonates and bicarbonates of the alkali metals are obtained by means of such reactions; they are soluble in water. The carbonates of other metals are insoluble in water, but the bicarbonates are soluble. Thus $CaCO_3$ is insoluble, but $CaH_2(CO_3)_2$ is soluble.

The insoluble carbonates may be obtained (1) by the addition of alkaline carbonates to a soluble salt of the metal—

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2\ NaCl;$$

(2) by passing carbon dioxide into a solution of the hydrate—

$$CaH_2O_2 + CO_2 = CaCO_3{}^{*} + H_2O.$$

Weak bases such as alumina, oxide of silver, and oxide of mercury either form no carbonates or very unstable ones, and the normal carbonates of the alkali metals are the only ones which withstand a high temperature without decomposition. All other carbonates when heated give off carbon dioxide and form an oxide of the metal (except ammonium carbonate which decomposes into ammonia, carbon dioxide and water).

313. **Test for Carbonates.**—Add dilute hydrochloric acid to the solid carbonate, or an aqueous solution of a carbonate in a test-tube. An effervescence will be observed, and on decanting the gas downwards into a second tube containing lime-water, and shaking up, a turbidity will be produced in the lime-water owing to the formation of calcium carbonate.

Distinction between Normal Carbonates and Bicarbonates.—The test just given applies to both normal carbonates and bicarbonates. If, however, the carbonate is insoluble in water, it must be a normal salt. If it is soluble the following tests will decide to which class it belongs :—

(1) Add magnesium sulphate to the solution. Normal carbonates give an immediate white precipitate; bicarbon-

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[*] Excess of CO_2 transforms this into the soluble bicarbonate—

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

ates only give a precipitate on boiling. (How do you explain this difference?)

(2) Add mercuric chloride to the solution. Normal carbonates give a reddish precipitate; bicarbonates give no precipitate.

CARBON BISULPHIDE, CS_2.

314. This compound occurs in traces in coal gas, and is formed in quantity when sulphur vapour is passed over red-hot charcoal. It is a colourless liquid, which refracts light strongly; it is very volatile, boiling at 46° C. and giving off a very inflammable vapour. When pure it has a sweetish, ethereal smell, but usually the impurities which it contains render it very disagreeable. One of its most remarkable properties is its solvent action; india-rubber, fats, and some of the non-metallic elements such as phosphorus, sulphur and iodine, which are otherwise difficult to obtain in solution, are readily dissolved by bisulphide of carbon.

In consequence of its high refractive power for light, it is frequently employed as a means of producing a spectrum, the liquid being introduced into a hollow glass prism.

CS_2 is the analogue in composition of CO_2, and thiocarbonic acid (H_2CS_3), the analogue of carbonic acid (H_2CO_3) is known; CS corresponding to CO has also been obtained. Thus a number of bodies are known containing sulphur in place of oxygen, the sulphur compound resembling the corresponding oxygen compound in chemical properties.

QUESTIONS.—CHAPTER XXIII.

1. Mention some conditions under which carbon monoxide is produced during the combustion of fuel on the large scale.
2. You desire to collect a specimen of CO as free as possible from air or CO_2, using oxalic acid as the source of the gas; how would you proceed?

3. What is the action of sulphuric acid on potassium formate? Give the equation.
4. What is the action of dilute and of concentrated sulphuric acid on potassium ferrocyanide?
5. How may CO be transformed into CO_2 and CO_2 into CO?
6. What is "generator gas," and how is it made? How would you show that it contains (*a*) CO, (*b*) CO_2, (*c*) H?
7. What is *water-gas*, and how is it manufactured?
8. It has been shown that chemical action undergoes modification when the reacting substances are perfectly dried; give instances of this.
9. How would you prove that carbon monoxide has the composition indicated by the formula CO?
10. What experiments would you perform in order to distinguish between

    (*a*) CO and CO_2;
    (*b*) CO_2 and a mixture of CO and CO_2 containing large excess of CO_2;
    (*c*) CO and a mixture of CO and CO_2 containing large excess of CO?

11. Write a short history of carbon dioxide.
12. Describe the reactions which take place when sodium bicarbonate ($NaHCO_3$) and lead carbonate ($PbCO_3$) are respectively subjected to the action of heat, and when they are brought into contact with dilute nitric acid.
13. Write down in separate columns (*a*) the physical, (*b*) the chemical properties of carbon dioxide.
14. Give two methods for the decomposition of carbon dioxide.
15. How may it be demonstrated that carbon dioxide has the formula CO_2?
16. Are there any grounds for the assumption that H_2CO_3 represents the composition of carbonic acid?
17. How are carbonates in general formed? Given metallic zinc, lime and caustic potash, how would you prepare specimens of zinc carbonate, calcium carbonate and potassium carbonate?

18. By what tests can *normal* carbonates be distinguished from *acid* carbonates?
19. What are the *characteristic* properties of bisulphide of carbon? What are the products formed, and their relative volumes, when this body is burnt in oxygen?
20. 15 c.cs. of carbon monoxide were exploded with 20 c.cs. of oxygen. After treating the product with excess of caustic potash 12·5 c.cs. of gas remain. Deduce from this the formula for carbon monoxide assuming carbon dioxide to be represented by CO_2.

SECTION III.—SYSTEMATIC STUDY OF SOME METALS.

CHAPTER XXIV.

MOLECULAR AND ATOMIC WEIGHT DETERMINATION.

315. Determination of Molecular Weight.—It has been shown that a molecule of hydrogen contains two atoms; therefore, the atomic weight of hydrogen being taken as unity, its molecular weight is 2. From Avogadro's theory, that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, it follows that the density of any gas compared with hydrogen is half the molecular weight of the gas. For—

$$\frac{\text{Density of gas}}{\text{Density of H}} = \frac{\text{Weight of } n \text{ molecules of gas}}{\text{Weight of } n \quad ,, \qquad ,, \quad \text{H}}$$
$$= \frac{n \times \text{mol. wt. of gas}}{n \times \text{mol. wt. of H}}$$
$$= \frac{\text{mol. wt. of gas}}{2}.$$

The most direct method, then, of determining the molecular weight of a substance is to find its density in the gaseous condition. If the substance is a gas at the ordinary temperature, its density may be found directly by weighing a globe of the gas. If the substance is liquid or solid at ordinary temperatures, it must be vaporized by heat. Four quantities must then be measured, *i.e.* the weight, volume, temperature, and pressure of a given quantity of the vapour. From these data the density of the vapour can be calculated. The chief practical methods employed in the determination of vapour densities are those of Dumas and Victor Meyer.

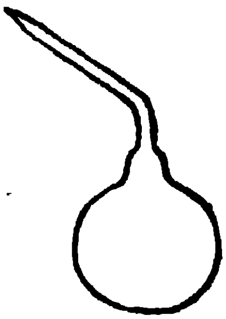

FIG. 76.

316. **Dumas' Method.**—A light glass bulb of about 200 c.c. content is drawn out to a fine point in the form shown in the figure, and weighed. This gives the weight of the bulb (w) filled with air, temperature and barometric pressure being noted. By gently warming the bulb, and then placing the orifice beneath the surface of the liquid whose vapour density is to be determined, and allowing the bulb to cool again, a quantity of the liquid is introduced. This should be in considerable excess of that required to fill the whole bulb with vapour, as it is necessary to ensure the air being expelled from the bulb in the process of volatilization; usually 5 to 10 cubic centimetres will suffice. The bulb is now placed in a bath of heated liquid, the temperature of which is kept constant, and at least 20° above that of the boiling point of the liquid under examination. When it is seen that the whole of the liquid has been transformed into vapour, the orifice of the bulb is sealed at the blow-pipe. We have now, presumably, the glass bulb quite filled with the vapour; after cooling and carefully cleaning, it is weighed. This gives the weight of the bulb ($w_{,}$) with the vapour required to fill it at the temperature of the bath.

The end of the sealed tube is then broken off under water; the water rushes in and should completely fill the bulb. The latter is now again weighed, along with the piece broken off. This gives the weight of the bulb ($w_{,,}$) filled with water.

$w_{,,} - w$ may be taken as the weight of water which has entered the bulb.[1] The internal volume of the bulb, therefore, is $w_{\prime\prime} - w$ c.c. The weight of this volume of air is

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[1] This is not quite exact, as w is not the weight of the bulb alone, but that of the bulb filled with air. The error so introduced, however, is quite negligible compared with the errors of experiment, and with the deviations from the gas-laws exhibited by vapours not far above their condensing points.

$$\frac{(w_{\prime\prime} - w) \times \cdot 001293 \times 273 \times p}{(273 + t) \times 760.} \text{ grammes,}$$

where p and t are respectively the pressure (in mm. of mercury) and the Centigrade temperature at the first weighing, and ·001293 the density of air at 0° C. and 760 mm. pressure (N.T.P.). If the weight of air so found is x, then the weight of the *vacuous* bulb is $w - x$. Hence the weight of vapour contained in the bulb at the second weighing is $w_{\prime} - (w - x)$, or $w_{\prime} - w + x$.

This weight of vapour has a known volume—that of the bulb, $w_{\prime\prime} - w$; it was measured at a known temperature—that of the bath; and at a known pressure—that of the atmosphere at the time of experiment. From these four data the weight of 1 c.c. of the vapour at 0° C. and 760 mm. pressure can be calculated. The result, divided by ·00009 (the weight of 1 c.c. of hydrogen at 0° C. and 760 mm.), gives the vapour density of the substance.

Several minor corrections have been omitted in the foregoing description, but they affect the result very slightly, and it must be remembered that a high degree of accuracy cannot be attained by this method, and is indeed unnecessary, since the main purpose in view is to decide whether the molecular weight of a given substance be M or some multiple or submultiple of M.

Dumas' method cannot be used at any temperature near that at which glass begins to soften (say over 400°), and is thus only applicable to liquids of low boiling point.

By substituting porcelain or metal for glass, as has been done by Deville and Troost and others, and heating the bulb in the vapour of sulphur (448°) or stannous chloride (606°) or other substances, the method is more widely applicable; by means of a gas furnace a temperature of 1700° has been attained and the vapour density of some metals such as zinc and cadmium, and of many salts such as aluminium chloride, ferric chloride, etc., has been determined. There is no essential difference in the nature of the observations to be made, though where a gas furnace is used, some means must be adopted for regulating and for measuring the temperature employed, and in addition to this it is desirable to replace the air in the bulb by nitrogen or some inert gas, since at high temperatures oxygen in most cases attacks the substance.

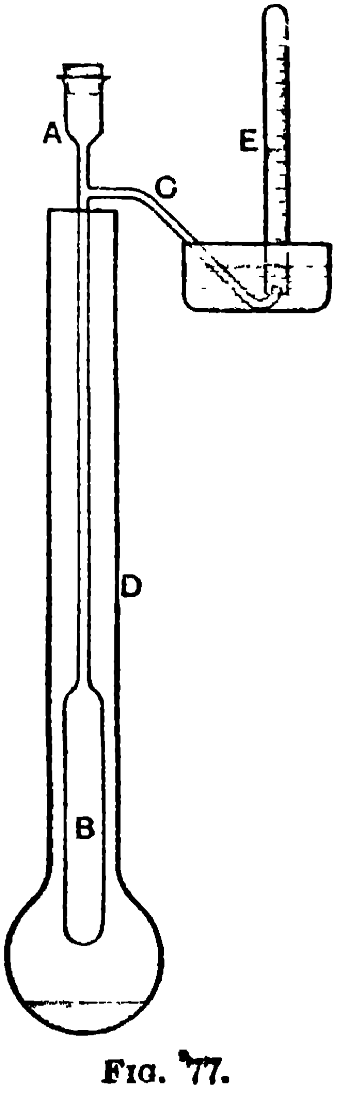

FIG. 77.

317. Victor Meyer's Method.—This is the only other method of importance used in the examination of inorganic bodies, and it possesses the advantage of being applicable over a considerable range of temperature; it is also easy to manipulate, and the determination can be made with a small quantity of the substance.

Fig. 2 represents the apparatus (supports omitted). It consists of a glass tube, AB, wide at the bottom, then narrow, and finally wide again near the top so as to admit an indiarubber stopper, the whole length of the tube being 600 mm. Near the top of the narrow portion there is a side tube, C, of the form shown. Surrounding the tube AB is a wider tube, D, containing a quantity of water, naphthalene, or other substance suitable for heating the glass bulb, according to the temperature required to volatilise the substance under examination, the bulb being so placed as to leave a clear space round it. A graduated tube (E) is filled with water and inverted over the end of the side tube. The cork being inserted in its place the jacket is heated and the temperature of the glass tube raised in this way to that of the vapour of the bath, 100° (water) or 217° (naphthalene), etc., as the case may be. Owing to the expansion of the air, bubbles pass out into the graduated tube.

When the temperature becomes constant the bubbles cease, and the cork is then withdrawn and a weighed amount (about 0·1 to 0·2 gramme) of the substance in a small bottle or bulb is dropped in* and the cork immediately replaced. If the experiment is successful, the substance will be very rapidly vaporised, and an equivalent volume (v) of air will be expelled through the side tube. This is carefully measured in cubic centimetres, and the temperature (t) and pressure (p) of the room at the time is noted. Reduced to standard temperature and pressure this will give the volume (V) which the vapour would occupy at standard temperature and pressure thus—

$$V = \frac{v \times 273 \times (p - s)}{(273 + t) \times 760},$$

s being the tension of aqueous vapour at the temperature t. This is the volume occupied by the weight (w) of the substance taken, when transformed into vapour, and it is easily seen that D the density compared with hydrogen will be

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* A little sand should be put in the bottom of the tube to prevent it being broken when the bulb is dropped in; also a device may be used by which the substance may be dropped into the tube without removing the cork.

$$D = \frac{w}{\cdot 00009 \times V}.$$

Provided only that the temperature of the jacket is constant and sufficiently high to ensure rapid vaporisation of the substance, the actual temperature employed need not be known. This will be clear if we remember that the volume of the air which is actually displaced and collected in the graduated tube is at the temperature of the room; the vapour of the substance occupies precisely the volume which this air would have occupied at the temperature of volatilisation. We have therefore the volume which the vapour would occupy if it could be collected at the temperature of the room.

318. **Determination of Atomic Weight.**—The accurate determination of the atomic weight of each of the elementary constituents of matter is of the utmost importance to the chemist, as no satisfactory classification of the facts of chemistry, as relating to compounds, can be made until the atomic weights of the elements have been decided upon.

Before proceeding to discuss the methods of atomic weight determination we must study the relationship which exists between the *atomic weight* of an element and its *chemical equivalent.*

319. **Relation between the Atomic Weight of an Element and its Equivalent.**—Now we have seen that the atomic weight of an element is the ratio of the weight of its atom to that of an atom of hydrogen, and the equivalent of an element is the weight of it which unites with or displaces 1 gramme of hydrogen.

It is clear then that since combination takes place between atoms of elements there must be a very close numerical relationship between the atomic weight of an element and its equivalent.

Let us consider the cases of a few elements, viz.: sodium, aluminium, chlorine, and oxygen.

The equivalents of these elements as determined experimentally are respectively 23, 9, 35·5, and 8. Their atomic weights (determined by methods which we shall investigate subsequently) are 23, 27, 35·5, and 16.

We have therefore for the numerical ratio $\frac{\text{Atomic Weight}}{\text{Equivalent}}$,

Sodium $\frac{23}{23} = 1.$

Aluminium $\frac{27}{9} = 3.$

Chlorine $\frac{35{\cdot}5}{35{\cdot}5} = 1.$

Oxygen $\frac{16}{8} = 2.$

In each of these cases then the atomic weight is either numerically equal to the equivalent or is a simple multiple of it.

If we had chosen other elements we should have obtained similar results, and the following general relation may be stated:—*The atomic weight of an element is numerically either equal to its chemical equivalent or is a simple multiple (rarely submultiple) of it.*

If you look up the valency of each of the elements considered above in the table in § 64 you will see that it is identical with the ratio $\frac{\text{Atomic Weight}}{\text{Equivalent}}$. A little reflection on the meaning of valency (§ 65) will enable you to realise that this must be the case, and that the following general relation between the atomic weight of an element and its equivalent may be stated—

$$\text{Valency} = \frac{\text{Atomic Weight}}{\text{Equivalent}}.$$

320. Deduction of Accurate Atomic Weights.—In order to find the accurate atomic weight of an element it is necessary to determine—

(1) The *accurate* value of the equivalent.
(2) An *approximate* value of the atomic weight.

Then the nearest multiple of the equivalent to the approximate value of the atomic weight gives the accurate atomic weight. [This multiple is obviously the *valency* of the element.]

Suppose, for example, the equivalent of an element is found to be 29·15, and an approximate determination of the atomic weight gives the number 60. Now $\frac{60}{29 \cdot 15} = 2$ approximately. Evidently the nearest multiple of the equivalent to 60 is 2, and the accurate atomic weight is 29·15 × 2 or 58·3. [Also the valency of the element is clearly 2.]

Methods of determining the equivalent of an element have been studied in § 57. We shall in the succeeding paragraphs study two methods of determining the approximate value of the atomic weight of an element.

321. The Vapour Density Method of Atomic Weight Determination.—This method consists in determining the vapour densities of as many compounds* of the element as possible, and deducing from them the molecular weights of the compounds as in § 315. These compounds are then analysed, and a table is drawn up showing in one column their molecular weights, and in another the weight of the element (deduced from the results of analysis) contained in the molecular weight of each compound.

It is found that the figures in the latter column are all simple multiples of the least number. *This smallest weight of the element contained in the molecular weight of any of its compounds is taken as the (approximate) atomic weight.* The atomic weight of the element cannot of course be greater than this number, though it might be less, since it is quite possible that each of the compounds whose molecular weight has been determined contains more than one atom of the element.

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* Also of the element itself if volatile.

Consider, for example, the case of carbon. A table constructed on the lines indicated shows the atomic weight to be 12.

Compound.	Molecular Weight.	Weight of Carbon in Molecular Weight.
Carbon monoxide	28	12
Carbon dioxide	44	12
Methane	16	12
Ethane	30	24
Acetylene	26	24
Propane	44	36
Butane	58	48
Benzene	78	72

The value found is in general only *approximate* because the vapour density of a substance as determined by the methods described in §§ 316, 317 is only approximately correct, and hence the value of the molecular weight deduced from it is only approximate. In the particular case considered, however, the value is an accurate one, because many of the compounds used are *gases*, and their densities can be determined accurately.

322. Determination of Atomic Weights by Application of Dulong and Petit's Law.—In the year 1819 Dulong and Petit published an account of a large number of determinations of the specific heat of solid bodies, particularly metals, and drew attention to the fact that these specific heats were in general inversely proportional to the atomic weight. There were notable exceptions, however, in the case of zinc, tin, lead, iron, and some other elements.

"Still," they say, "the mere inspection of the numbers obtained points to a relation so remarkable in its simplicity as to be at once recognised as a physical law, susceptible of being generalised and extended to all elementary substances. In fact, the products in question, which express the capacities for heat of atoms of different nature, are so nearly the same for all, that we cannot but attribute these very slight differences to unavoidable errors, either in the determination of capacities for heat or in the chemical analyses." They thus deduced from their observations the law that "the atoms of all simple bodies have precisely the same capacity for heat."

The adoption of this generalisation by chemists led to the alteration of a number of the then accepted values for atomic weight. This of course was followed by changes in the formulae of the compounds derived from these elements. In all instances, however, where revision has taken place the effect has been to bring out in a clearer light the relations which the elements and their compounds show to one another, and to throw them into natural groups, in which striking resemblances are shown between the members of the same group. It is on this ground that the generalisation of Dulong and Petit has appealed so strongly to chemists.

In the following table we give the atomic weights (A.) and specific heats (C.) of a number of the commoner elements, and also the product (A.C.) of the atomic weight multiplied by the specific heat (the so-called "atomic heat"), this being in most cases practically a constant, whose value is approximately 6·4.

	Atomic weight. A.	Specific heat. C.	Atomic heat. A.C.
Sodium ...	23·0	0·293	6·7
Magnesium ...	24·0	0·250	6·0
Aluminium ...	27·0	0·214	5·8
Phosphorus ..	31·0	0·174	5·4
Sulphur . .	32·0	0·178	5·7
Potassium ...	39·0	0·166	6·5
Calcium ...	39·9	0·170	6·8
Chromium ...	52·4	0·121	6·3
Manganese ...	54·8	0·122	6·7
Iron	55·9	0·114	6·4
Copper	63·2	0·095	6·0
Zinc	65·1	0·094	6·1
Arsenic ...	74·9	0·081	6·1

	Atomic weight. A.	Specific heat. C.	Atomic h A.C.
Bromine[*] (solid)	79·8	0·084	6·7
Silver	107·7	0·057	6·1
Tin	118·8	0·055	6·5
Antimony ...	119·6	0·051	6·1
Iodine	126·5	0·054	6·8
Platinum ...	194·3	0·032	6·3
Gold	196·7	0·032	6·4
Mercury[†] (solid)	199·8	0·032	6·4
Lead	206·4	0·031	6·4
Bismuth ...	207·3	0·030	6·4
Uranium ...	239·0	0·028	6·7

The above results may be regarded as consistent with Dulong and Petit's Law, which may be stated thus:—*The atomic weight of an element, multiplied by its specific heat in the solid condition, gives a result which approximates very nearly to* 6·4.

There are, however, notable exceptions, for which we have not yet accounted. The values of A.C. for carbon, boron, beryllium, and silicon are respectively 1·8, 2·7, 3·7, and 3·8.

Observations made by Weber in 1875, on the behaviour of carbon, boron, and silicon, have shown that the specific heat of these elements increases as the temperature rises, and at a certain limit it remains almost constant through a considerable range of temperature, thus—

from 800° C. to 980° C. A.C. for carbon = 5·5
at 600° C. „ boron = 5·5
from 130° C. to 250° C. „ silicon = 5·7

Also Humpidge found similarly the value of A.C. for beryllium to be 5·6 at 400° C. to 500° C.

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[*] The specific heat of bromine in the ordinary liquid state is considerably higher than the value given here.

[†] The specific heat of mercury in the liquid state is higher than the value given here.

It should be noted that all these apparent exceptions are elements of low atomic weight and very high melting points. Elements with atomic weights over 30 obey Dulong and Petit's Law, practically without exception.

The fact must be emphasised that Dulong and Petit's Law only gives *approximate* values for atomic weights, *i.e.* it enables us to determine what value of the equivalent of an element is to be taken as its *accurate* atomic weight.

As an example of the application of the Law, let us consider the case of uranium. The analysis of uranium chloride shows that 60 grammes of uranium unite with 35·5 grammes of chlorine. Therefore the equivalent of uranium is 60.

Now the specific heat of this element has been found to be 0·028.

Applying Dulong and Petit's Law, we have

$$\text{Sp. Ht.} \times \text{At. Wt.} = 6{\cdot}4$$
$$0{\cdot}028 \times \text{At. Wt.} = 6{\cdot}4$$
$$\text{At. Wt.} = \frac{6{\cdot}4}{0{\cdot}028} = 229.$$

The approximate value of the atomic weight of uranium is therefore 229.

Now

$$\frac{229}{60} = 4$$

correct to the nearest whole number.

Therefore the nearest multiple of the equivalent of uranium to its approximate atomic weight as deduced from the specific heat is 4, and the accurate value of the atomic weight of the element is 4 × 60, or 240.

It should be pointed out finally that Dulong and Petit's Law may be applied to determine whether the maximum value for the atomic weight of an element determined as in § 321 is the correct value or a multiple of it.

QUESTIONS.—CHAPTER XXIV.

1. Describe two methods of determining the vapour density of a substance at temperatures higher than atmospheric.
2. Calculate the molecular weight of chloroform from the following data obtained by Dumas' method:—Capacity of bulb = 127 c.c.; temperature of bath, 136° C.; weight of vapour = 0 4524 gramme.
3. Show why a knowledge of the vapour density of a body is of value in fixing its molecular weight.
4. What is Dulong and Petit's Law, and of what value is it to the chemist?
5. If the specific heat of an element be 0·21, and its chemical equivalent be 9, what multiple of the latter should be taken as the atomic weight?
6. Explain the vapour density method of atomic weight determination.
7. In an experiment it was found that 0·5 gramme of zinc displaced 1·66 gramme of silver from a solution of silver nitrate.

   Given that the chemical equivalent of zinc is 32·5 and the specific heat of silver 0·057, calculate the atomic weight of silver.
8. The specific heat of platinum is 0·0324, what should be its approximate atomic weight?
9. How far do beryllium, boron, carbon, and silicon conform to Dulong and Petit's Law?

CHAPTER XXV.

PHENOMENA OF ELECTROLYSIS.

323. Some examples of Electrolysis have already been met with incidentally in the preceding chapters, but the more obvious phenomena of electrolysis should be studied more systematically. In the following explanations some knowledge of the elements of electricity is assumed.

Electrolysis of Copper Sulphate.—

Exp. 194.—Fit up an apparatus similar to that used in Exp. 46. Pour some copper sulphate solution into the bottle and pass a current from two or three Grove's cells through the liquid. You will observe that gas bubbles arise only from the *positive* electrode (*i.e.* piece of platinum foil connected with the *positive* or *platinum* pole of the battery); the *negative* electrode (*i.e.* the piece of platinum foil connected with the *negative* or *zinc* pole of the battery) becomes covered with a red coating of *metallic copper*. Collect some of the gas evolved at the positive electrode in a test-tube by displacement of water and test it with a glowing splint: it is *oxygen*.

We see then that when an electric current is passed through a solution of copper sulphate, using platinum electrodes, oxygen is evolved at the positive electrode and copper set free at the negative electrode. It is found further that sulphuric acid gradually accumulates in the liquid.

Such an action—the decomposition of a liquid by an electric current—is called *electrolysis*, and the liquid is called the *electrolyte*. The vessel in which the decomposition takes place is called the *electrolytic cell.*

The course which the current takes during its circuit is as follows:—Starting from the positive (platinum) pole it flows along the connecting wire to the positive electrode (which is called the *anode*), thence through the liquid to the negative electrode (called the *kathode*), and finally back to the battery along the other connecting wire.

The following explanation of the phenomenon investigated in Exp. 194 is at present generally accepted.

It is supposed that when copper sulphate ($CuSO_4$) is dissolved in water, some (in dilute solution the greater part) of the molecules are dissociated into two "ions." The one ion is the atom Cu, and the other is the group of atoms SO_4, which is called *sulphion*. The ion Cu is supposed to carry a *positive* charge of electricity and the ion SO_4 a *negative* charge. When the electrodes are introduced into the liquids they attract the charged ions; the negative electrode attracts the positively charged ions, *i.e.* the copper ions, and the positive electrode attracts the negatively charged ions, *i.e.* the sulphions. This is in accordance with the ordinary law of electric attraction. There is consequently a stream of Cu ions proceeding towards the negative electrode, and a stream of SO_4 ions proceeding towards the positive electrode. This is represented diagrammatically in Fig. 78, in which $\overset{+}{Cu}$ stands for a positively charged copper ion, and $\overset{-}{SO_4}$ stands for a negatively charged sulphion.

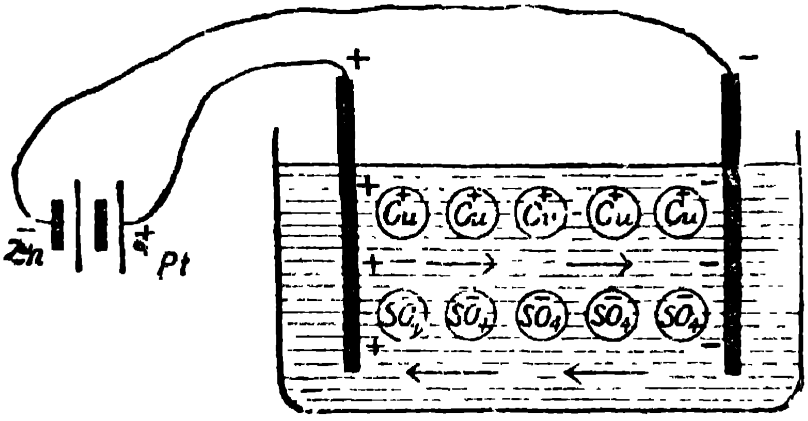

FIG. 78.

When a Cu ion reaches the negative electrode it gives up its electric charge, and is deposited on the electrode as a thin film. At the same time an SO_4 ion reaches the positive electrode and gives up its charge. An uncharged sulphion is, however, incapable of a separate existence, and immediately reacts with the water in contact with the positive electrode, with formation of sulphuric acid and liberation of oxygen.

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

The ion Cu, which is attracted to the kathode, is called the *kathion*; and the ion SO_4, which is attracted to the anode, is called the *anion*.

324. Electrolysis in General.—The process of electrolysis is very general in its application. All acids, alkalies, and salts in solution are electrolytes to a greater or less extent; that is to say, they can be decomposed by an electric current. In the case of salts, the kathion (or kathions) consists of the atom (or atoms) of metal in the molecule, the remainder of the molecule forming the anion. In the case of acids, the kathion (or kathions) consists of the atom (or atoms) of hydrogen in the molecule. The presence of these hydrogen ions may be considered to be the cause of the acidity of the solution.

The properties of elements in the state of ions are different from their properties in the ordinary unionised state: *e.g.* ionic sodium does not decompose water. But when the ions reach the electrodes their charge is neutralised, and they resume their normal chemical properties. Hence it frequently happens that further chemical action takes place at one or both electrodes between the discharged ions and the liquid or the metal of which the electrodes are composed.

325. Electrolysis of Water.—Pure water does not conduct electricity, but when an acid, base, or salt is dissolved in it, it becomes an electrolyte.

An experiment in which water acidulated with dilute sulphuric acid is decomposed by the electric current has-already been described (Exp. 47). The part played by the sulphuric acid is explained as follows:—The acid on solution dissociates into three ions, two of hydrogen (H) and one of sulphion (SO_4). The hydrogen ions carry positive charges of electricity and the sulphion a negative charge.* On passing the current, the H ions are attracted to the negative electrode, where they give up their charge and acquire the properties which we ordinarily associate with hydrogen. One of these is that free atoms of hydrogen cannot exist separately; they therefore combine to form molecules, in which form the gas passes off and may be collected. The sulphions are attracted to the positive electrode, and after giving up their charges undergo a secondary reaction with water with liberation of oxygen, as already described in the previous paragraph.

Let us start with, say, two† molecules of sulphuric acid, and trace the changes which they undergo. We may represent the primary change which takes place on passing the current by the equation

$$2H_2SO_4 = 2H_2 + 2SO_4.$$

The $2H_2$ is evolved at the kathode and the $2SO_4$ liberated at the anode reacts with water thus—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

The O_2 is evolved at the anode.

We therefore finish with the same amount of sulphuric acid with which we started, *i.e.* 2 molecules, and the net result of passing the current has been to break up two molecules of water into two molecules of hydrogen and one molecule of oxygen. The same result would have been arrived at if we had taken any other number of sulphuric acid molecules, from which it follows that the amount of sulphuric acid in the cell remains unchanged, and the gases ultimately liberated are the constituents of pure water.

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* The negative charge carried by the sulphion is *twice* as large as the positive charge carried by each of the hydrogen ions, so that the total charge on the three ions into which the molecule of sulphuric acid dissociates is equal to zero.

† *Two* molecules are used instead of one to avoid writing an *atom* of oxygen in the second equation.

326. **Electrolysis of Hydrochloric Acid.**—If strong hydrochloric acid be substituted for dilute sulphuric acid the ions are hydrogen and chlorine. On passing the current, hydrogen at once appears at the kathode, but no chlorine makes its appearance, for two reasons: firstly, because chlorine is soluble in the acid solution; and, secondly, because the chlorine, while still in the condition of free atoms (*nascent* chlorine), attacks the platinum anode, converting it into the soluble platinum chloride ($PtCl_4$). If the anode be a plate of gas carbon, on which chlorine, even when nascent, has no action, and if the solution be saturated with chlorine beforehand, hydrogen and chlorine appear in equal volumes, as we saw in Exp. 123.

327. **Electrolysis of Solutions of Alkalies.**—When caustic soda ($NaOH$) dissolves in water it separates into the two ions, sodium and hydroxyl (OH). On passing a current through the solution the former is liberated at the kathode and the latter at the anode. Neither of these, however, appears, because of secondary actions, the sodium immediately decomposing water with evolution of hydrogen and re-formation of caustic soda, and two of the hydroxyl groups breaking up into oxygen, which escapes, and water, which remains. Considering the changes which four* molecules of caustic soda undergo we have as the primary change on passing the current—

$$4NaOH = 4Na + 4OH.$$

The following secondary changes then take place. At the kathode—

$$4Na + 4H_2O = 4NaOH + 2H_2;$$

at the anode—

$$4OH = 2H_2O + O_2.$$

The net result is that the amount of caustic soda remains unchanged and water is decomposed into hydrogen and oxygen. It will therefore be seen that the electrolysis of dilute sulphuric acid and of caustic soda solution both bring about the same result, namely, the decomposition of water.

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* Four molecules are used for a similar reason to that referred to in the foot-note on p. 366.

All alkalies give *hydroxyl ions* when dissolved in water, and these may be considered as the cause of the alkalinity of the solution.

328. **Electrolysis of Solutions of Salts.**—Here the immediate products of the decomposition (ions) are the metal and the acid radicle—SO_4, Cl, NO_3, etc.—the former, like the metal of an alkali and the hydrogen of an acid, always going to the kathode, and the latter always going to the anode when the current is passed. But whether these ions actually appear or not after giving up their charges to the electrodes depends upon the nature of the ions and the presence or absence of secondary actions between them and the liquid or the electrodes.

Except in the case of those metals which decompose water at the ordinary temperature (sodium, etc.), the metal[1] is always deposited on the kathode; but, except in the case of some of the hydracids (hydrochloric acid, hydriodic acid, etc.), the acid radicle rarely appears as such, even if no action takes place between it and the anode. In the case of nitrates, for example, the radicle NO_3 reacts with water, yielding nitric acid and oxygen—

$$4NO_3 + 2H_2O = 4HNO_3 + O_2.$$

If a solution of zinc sulphate ($ZnSO_4$) be electrolysed between platinum electrodes, zinc is deposited on the kathode, and for every atom of zinc deposited an atom of oxygen is liberated at the anode and a molecule of sulphuric acid goes into solution. But if a plate of zinc replace the platinum anode, the SO_4 group, instead of reacting with water, simply combines with the zinc to form zinc sulphate. Then for every molecule of zinc sulphate decomposed, and for every atom of zinc deposited at the kathode, an atom of zinc is dissolved and a molecule of zinc sulphate re-formed at the anode; so that the kathode gains exactly as much zinc as the anode loses, and the average composition of the solution remains unaltered.

With copper sulphate ($CuSO_4$) electrolysed between copper electrodes the action is less simple. Copper is deposited on the kathode, but at the anode some of the SO_4 directly unites with the copper to re-form copper sulphate, and some reacts with water forming sulphuric acid, with liberation of oxygen. And of this oxygen some escapes, while some unites with the copper to form copper oxide (CuO), which in part incrusts the plate, and in part dissolves in the acid with re-formation of copper sulphate—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

329. **Double Salts.**—This is a convenient place at which to briefly discuss the nature of *double salts.* These are complex salts formed by the union of two simple salts, *e.g.* a molecule of potassium sulphate, K_2SO_4, and one of aluminium sulphate, $Al_2(SO_4)_3$, together with 24 molecules of water, unite together to form a molecule of potassium aluminium sulphate or alum—

$$K_2SO_4,\ Al_2(SO_4)_3,\ 24H_2O.$$

Double salts may be divided into two classes, according to their behaviour in solution. Some break up into the simple salts of which they are composed, and these then decompose further into ions in the usual way; thus alum breaks up into K_2SO_4 and $Al_2(SO_4)_3$, and these salts then yield the ions K, Al, and SO_4. Others do not decompose in this way, but ionise immediately, yielding a complex anion containing one of the metals; for example, potassium chloride, KCl, unites with platinum chloride, $PtCl_4$, to form the double salt $2KCl + PtCl_4$ or K_2PtCl_6; on dissolving this salt in water the kathions consist of K and the anions of the complex group $PtCl_6$. This salt may therefore be considered to be derived from the acid H_2PtCl_6, chloroplatinic acid, and is called potassium chloroplatinate.

Other examples of the first class of double salts are carnallite, KCl, $MgCl_2$, $6H_2O$, and ferrous ammonium sulphate, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$, and of the second class, potassium ferrocyanide, $K_4FeC_6N_6$, which yields the complex anion FeC_6N_6.

330. Faraday's Laws of Electrolysis.—Faraday discovered two very important laws connected with the quantities of elements set free at the electrodes during electrolysis. They may be stated as follows:—

1*st Law.*—The quantity of an element set free during a given time is proportional to the strength of the current.

2*nd Law.*—The quantities of the elements deposited in the same circuit are in the ratio of their chemical equivalents.

The second law affords a very useful method of determining chemical equivalents of metals. For suppose the same current is passed successively through three electrolytic cells containing respectively (*a*) acidulated water, (*b*) a solution of silver nitrate, (*c*) a solution of copper sulphate, by connecting the cells in series with a battery as shown diagrammatically in Fig. 79 (the arrows indicate the direction of flow of the current). These cells form part of the same circuit, and according to Faraday's second law the weights of hydrogen collected and of silver and copper deposited on the kathodes are in the ratio of their chemical equivalents. In order, then, to find the equivalents of silver and copper, all that is necessary is to divide the weights of these elements deposited after passing the current for a suitable time by the weight of hydrogen evolved.

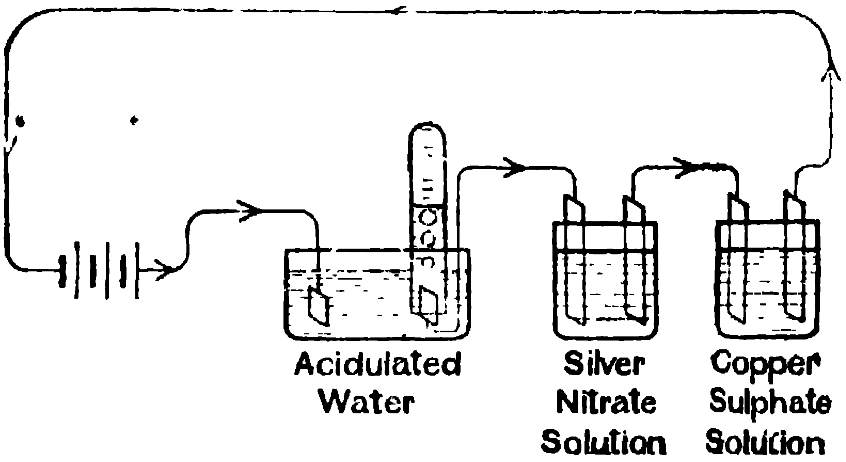

Fig. 79.

Suppose for example the weights were as follows:—

Hydrogen	0·0104	gram.
Silver	1·123	grams.
Copper	0·328	gram.

Then we have—

$$\frac{\text{Chemical Equivalent of Silver}}{\text{Chemical Equivalent of Hydrogen}} = \frac{1{\cdot}123}{0{\cdot}0104}.$$

$$\therefore \frac{\text{Chemical Equivalent of Silver}}{1} = \frac{1{\cdot}123}{0{\cdot}0104}.$$

$$\text{Chemical Equivalent of Silver} = 108.$$

Similarly—

$$\frac{\text{Chemical Equivalent of Copper}}{\text{Chemical Equivalent of Hydrogen}} = \frac{0{\cdot}328}{0{\cdot}0104}.$$

$$\therefore \text{Chemical Equivalent of Copper} = 31{\cdot}5.$$

If the equivalent of one metal is known, all that is necessary in order to find the equivalent of a second is to include cells containing salts of each in the same circuit and find the increase in weight of the kathodes after a suitable time.

Suppose, for example, the equivalent of silver is known to be 108 and the weights of silver and copper deposited when the same current is passed through solutions of silver nitrate and copper sulphate are 2·14 grams and 0·63 gram. Then we have—

$$\frac{\text{Chemical Equivalent of Copper}}{\text{Chemical Equivalent of Silver}} = \frac{0{\cdot}63}{2{\cdot}16}.$$

$$\therefore \frac{\text{Chemical Equivalent of Copper}}{108} = \frac{0{\cdot}63}{2{\cdot}16}.$$

$$\text{Chemical Equivalent of Copper} = \frac{0{\cdot}63}{2{\cdot}16} \times 108$$

$$= 31{\cdot}5.$$

It should be noted that the equivalent of copper found above is its equivalent *in copper sulphate*, i.e. in the *-ic* state. If a solution of a *cuprous* salt (say cuprous chloride dissolved in hydrochloric acid) were used, the equivalent would be found to be twice as great, *i.e.* 63. A similar remark applies to other elements which form -ous and -ic salts.

331. **Useful Applications.—Electro-depositions.**—The principle of electrolysis has many useful applications in the arts. One of the oldest of these is the process of *electro-plating*. Here the object to be plated is thoroughly cleaned and slightly roughened, and made the kathode of an electrolytic cell, the anode being a plate of the metal to be deposited, and the electrolyte a solution of a salt of that metal, the current being supplied by a battery or dynamo. A thin and firmly adherent film of the metal —gold, silver, nickel, or what not—is deposited on the article to be plated, and the strength of the solution is kept up by the action of the electrolyte on the anode. Compare with this the above description of the electrolysis of zinc sulphate, when a zinc anode is used.

The most important electro-plating industry is electro-*silvering*. In this case the salt is a double cyanide* of silver and potassium, the "bath" being prepared by dissolving one part (by weight) of silver cyanide and two of potassium cyanide in 40 of distilled water. The current is maintained until the deposit amounts to about one ounce per square foot, which corresponds to a thickness of about $\frac{1}{600}$ inch.

Electro-*gilding* is the art of coating objects with gold. The bath is a solution of the double cyanide of gold and potassium. The details are similar to those for electro-silvering, except that the current employed is weaker and the deposit thinner.

Electro-*nickeling* is the art of coating objects (usually of steel, such as the handle-bars of bicycles) with nickel. The bath is a slightly acid solution of the double sulphate of nickel and ammonium. A good coat consists of about $\frac{2}{3}$ ounce per square foot, which represents about $\frac{1}{1000}$ inch in thickness.

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* Cyanides are derived from hydrocyanic acid, HCN.

Electro-*coppering* is the easiest of all the plating processes. The bath is simply a strong and very slightly acid solution of copper sulphate. When *iron* is the metal to be coppered the simple copper sulphate bath is unsuitable, because the sulphate would be rapidly decomposed by the iron; in this case the bath consists of an alkaline solution of the double tartrate of copper and sodium obtained by adding excess of sodium hydroxide to a solution of copper sulphate and tartaric acid.

In *electrotyping*, the object is to produce not a thin adherent coat, but a thick one, which may be readily detached from the mould which serves as the kathode, and which reproduces, with the utmost fidelity, all the form and relief of the original article. Engraved wood blocks, for instance, are thus reproduced in copper. A mould is first prepared in gutta-percha, plaster of Paris, or some other substance. The face of this mould is then black-leaded to form a conducting film, and the mould is hung in a solution of sulphate of copper, in which it becomes the kathode, the anode being a sheet of copper suspended in the solution. When the deposited copper forms a layer of sufficient thickness it is removed from the mould, backed with type metal, and mounted type-high* on a wood block.

332. **Electrometallurgy.**—Many metals are now economically extracted from their compounds by electrolysis—sodium, for instance, the electrolyte being caustic soda melted by heat. Sodium and hydrogen separate at the kathode (the latter being allowed to escape), and oxygen at the anode. Aluminium, is similarly obtained by the electrolysis of alumina dissolved in a bath of molten fluorides of aluminium, sodium, and calcium. Crude copper is also economically refined by using it for an anode, and re-depositing it in a state of purity upon rods or sheets of copper which serve as kathodes. In these cases the current is derived from a dynamo driven by steam- or water-power.

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* *I.e.* the face is brought level with the face of the type.

QUESTIONS.—CHAPTER XXV.

1. Describe what you would observe on passing a current of electricity through aqueous solutions of the following substances, using platinum electrodes:—(1) copper sulphate; (2) sulphuric acid; (3) caustic potash.

2. Explain the meaning of the terms—*electrolysis, ion, anode, kathode.*

3. What do you understand by an *electrolyte?* Describe and explain as far as you can what takes place when an electric current is passed through (i) a solution of caustic soda, (ii) fused caustic soda.

4. Describe and explain what takes place when a current of electricity is passed through a solution of zinc sulphate between platinum electrodes.

5. The same electric current is passed through solutions of copper sulphate and stannic chloride. What will be the relationship between the weights of metals deposited, and what law do they illustrate?

6. Give Faraday's Laws of Electrolysis, and explain how you would prove them.

7. Describe a method of determining the *chemical equivalent* of copper by means of electrolysis.

8. Write a short account of the applications of the principle of electrolysis which have been made in the arts.

9. What are double salts? Into what two classes can they be divided? Illustrate your answer by examples.

CHAPTER XXVI.

SODIUM.

333. **Occurrence.**—

(1) As common salt, NaCl, in sea-water, and some inland lakes, and in lenticular deposits in rocks, more especially in the strata of the age of the New Red Sandstone.

(2) As nitrate (Chili saltpetre) in the west of South America.

(3) Occasionally in springs or inland lakes as sulphate, carbonate, or borate.

(4) In many mineral silicates.

The two first sources afford the principal supply of the raw material for the production of sodium salts.

334. **Preparation of the Metal.**—Sodium was prepared on a large scale by heating carbon with sodium carbonate.

$$Na_2CO_3 + 2C = 2\ Na + 3\ CO.$$

Castner improved on this process by replacing sodium carbonate by caustic soda—

$$6\ NaOH + 2C = 2\ Na + 2\ Na_2CO_3 + 3H_2.$$

Electrolytic Method: Discovery of Sodium.—The above methods have now been almost entirely displaced by electrolytic methods. Until quite recently fused caustic soda was used exclusively as the electrolyte, but now fused sodium chloride is taking its place to a large extent. It is interesting to notice that when caustic soda is employed the method is identical in principle with that employed by Davy, the discoverer of sodium and potassium. Davy first isolated potassium and afterwards employed the same method for sodium.

He placed upon an insulated disc of platinum a small piece of pure caustic potash, which had been exposed to the air for a few seconds, during which time it became deliquescent on the surface and was then in a condition to conduct the current. The disc constituted the negative electrode and a platinum wire connected with the positive pole completed the circuit when brought into contact with the upper surface of the potash. The whole apparatus was in the open air.

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrisation. There was a violent effervescence at the upper surface; at the lower, or negative, surface there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame as soon as they were formed, and others remained or were quickly covered by a white film which formed on their surfaces."*

These globules were potassium. Sodium was immediately afterwards obtained in a similar way, though Davy found that soda was not so readily decomposed as potash. He found it impossible to obtain, with his battery of 100 cells, pieces of sodium of more than fifteen or twenty grains in weight.

335. **Castner's Electrolytic Process.**—The apparatus now employed for the electrolysis of caustic soda, due to Castner, consists essentially of a cylindrical iron pot, A (Fig. 80), containing the fused caustic soda which is kept at a temperature of not more than 20° above its melting point. Passing up through the base of the pot is a metal rod, D, which is connected with the negative pole of a dynamo. It is sealed into the narrow continuation, M, of the pot by means of melted caustic soda, which has been allowed to solidify (F). The anode is a metal cylinder, B, which forms part of the cover of the pot, and is connected with the positive pole of the dynamo by means of G. The cover is insulated from the pot by a pad of asbestos, K K.

The current passes through the annular space between the anode and the kathode, and it is here that the decomposition takes place. Sodium and hydrogen are liberated at the kathode and rise through the caustic soda into a cylindrical receptacle, C, which is fastened to the cover of the pot. To the lower end of C is adapted a wire gauze cylinder, *p*, which surrounds the kathode, and prevents the sodium from rising otherwise than into C. The sodium (E) collects on the surface of the caustic soda (in virtue of its lower specific gravity) and is removed periodically by a perforated ladle, which allows the molten caustic to flow back into the vessel. The hydrogen escapes under the edges of the lid of C. Oxygen is evolved at the anode and escapes through a hole in the lid of A.

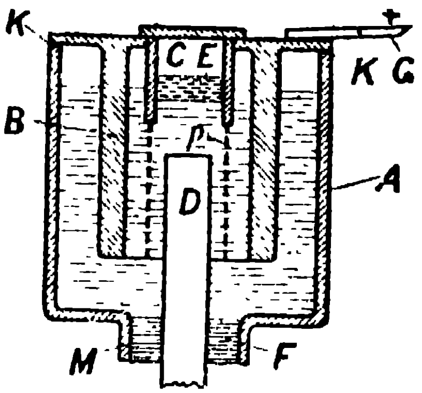

FIG. 80.

336. **Properties of Sodium.**—Sodium is a soft malleable metal of specific gravity 0·974; it shows a silvery lustre when freshly cut, but rapidly tarnishes through oxidation, even at ordinary temperatures. It melts at 95·6° C., and is transformed into a violet vapour at about 740° C. It burns vividly in oxygen and in chlorine, though these gases have no action upon it when perfectly dry. Like potassium it decomposes water at the ordinary temperature, the heat generated in the reaction being insufficient to ignite the hydrogen (as it does in the case of potassium); if the sodium be, however, brought into contact with hot water, or water thickened with starch, the hydrogen in flames.

Metallic sodium was formerly of importance in the manufacture of aluminium, and is still used in the separation of magnesium, silicon, and boron. Sodium amalgam is sometimes used instead of mercury alone in the extraction of gold and silver, and is employed in many reduction processes in organic chemistry.

337. Sodium Hydride, NaH.—This substance was first prepared by Moissan, and its formation subsequently confirmed by Holt. It is obtained when a slow current of pure hydrogen is passed over sodium placed in a nickel boat, and heated to about 350° C., an ordinary small combustion furnace being employed for the heating of the sodium. Colourless matted crystals form just beyond the boat resembling cotton-wool in appearance. They are decomposed by water, giving NaOH and hydrogen, a reaction which may be employed to determine the formula of the substance. The crystals undergo decomposition in moist air, and also when acted upon by HCl. Nitric and sulphuric acids and mercury have no action on sodium hydride.

338. **Oxides of Sodium.—Sodium Monoxide, Na_2O.**—Sodium does not oxidise in perfectly dry air or oxygen at ordinary temperatures, but if heated in moist oxygen a mixture of the monoxide and dioxide is formed. The monoxide has lately been obtained in a purer form by heating sodium with sodium nitrate in the proportions required by the equation

$$2\,NaNO_3 + 10\,Na = 6\,Na_2O + N_2.$$

The monoxide is described as a greyish mass which melts at a dull red heat and volatilises at a higher temperature. It combines readily with water, forming sodium hydroxide.—

$$Na_2O + H_2O = 2\,NaOH.$$

Sodium Dioxide, Na_2O_2, usually termed **sodium peroxide,** is a substance of some importance, and is formed by heating sodium in air or oxygen. It was first obtained pure by Harcourt, who prepared it by heating sodium in a hard glass flask till it melted, and then sending a slow current of dry air through the flask, the heating being continued till the product was a yellowish-white solid.

It is now prepared on a large scale by placing sodium on aluminium trays which are caused to pass, by a mechanical arrangement, through an iron tube heated to about 300° C., through which excess of air freed from moisture and carbon dioxide is continuously passed. About 93 per cent. of the product is Na_2O_2.

The pure compound is white, but the commercial product is usually somewhat yellow in appearance. The preparation of this substance on such a scale is a direct consequence of the production of sodium by the more rapid and less expensive methods of recent years.

Sodium peroxide is stable in dry air, at ordinary temperatures, and does not give off oxygen unless heated to a high temperature.

It decomposes water with evolution of oxygen—

$$2\,Na_2O_2 + 2\,H_2O = 4\,NaOH + O_2,$$

or, if the temperature is kept low, with formation of hydrogen peroxide—

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2.$$

In presence of dilute acids it yields hydrogen peroxide—

$$Na_2O_2 + 2\,H_2SO_4 = 2\,NaHSO_4 + H_2O_2.$$

Sodium peroxide is made on a large scale for the preparation of *soda bleach*, which is a solution of the dioxide in dilute hydrochloric acid; and therefore contains hydrogen peroxide. It is sold in the solid form for a similar purpose, mixed with $CaCl_2$ or $MgCl_2$, a mixture which yields with water H_2O_2 and the hydroxides of calcium and magnesium.

It is, as one would expect, a powerful oxidising agent and is used as such in the laboratory in the analysis of certain minerals such as iron pyrites and chrome ironstone.

Exp. 195.—Heat strongly in a nickel crucible an intimate mixture of 1 part finely-powdered chrome ironstone, $FeO.Cr_2O_3$, and 6 parts sodium peroxide for some time. Allow the fused mass to cool, extract with water, and filter. Observe the yellow filtrate, due to the formation of sodium chromate, and the reddish residue of ferric oxide. Note also the strongly alkaline character of the liquid.

$$2\,FeO.Cr_2O_3 + 7\,Na_2O_2 = Fe_2O_3 + 4\,Na_2CrO_4 + 3\,Na_2O.$$

339. Sodium Hydroxide or Caustic Soda, NaOH.—Caustic soda is prepared on a very large scale, being used in the making of soap and paper, for refining oils, and for many other purposes.

It is manufactured by boiling sodium carbonate solution with lime, when calcium carbonate is precipitated and caustic soda passes into solution—

$$Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2\,NaOH.$$

When the change is complete the mixture is allowed to settle and the clear liquor run off and evaporated till all the water has been driven off.* The fused caustic soda is then run into moulds, where it solidifies.

In actual practice the mother liquor which remains after the crystallisation of sodium carbonate from the "tank liquor" of the Leblanc process (see § 351) is employed. This liquor already contains some caustic soda† as well as sodium carbonate. A number of impurities present are removed as far as possible by suitable treatment.

Caustic Soda by Electrolysis.—Much caustic soda is now manufactured by the direct electrolysis of brine.

The primary action is of course the separation of sodium and chlorine—

$$NaCl = \overset{+}{Na} + \overset{-}{Cl}.$$

The sodium acts on the water—

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

It is of importance to prevent the caustic soda and the chlorine coming in contact, since they act on each other, and reproduce salt, the following reactions taking place:—

$$2\,NaOH + Cl_2 = NaClO + NaCl + H_2O.$$
$$3\,NaClO = NaClO_3 + 2\,NaCl.$$
$$NaClO_3 + \underset{\text{Nascent}}{6\,H} = NaCl + 3\,H_2O.$$

Porous diaphragms, chiefly of asbestos, have been used to prevent the diffusion of caustic soda and chlorine, but without much success. The apparatus of Castner and Kellner (Fig. 81), however, appears to have solved the problem. The brine chambers, BB, containing the carbon anodes, AA, are divided by partitions dipping into mercury from the central chamber containing the iron cathodes and caustic soda. In the outer chambers the mercury takes up sodium, forming an amalgam. The cell is given a slight rocking motion which carries the sodium amalgam into the central chamber. Here the amalgam acts as anode to the iron kathode; the sodium goes into solution as caustic soda and hydrogen is evolved at the kathode.

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* This may be tested by allowing a sample to cool, when it should solidify.

† Produced during the lixiviation of the *black ash* by the action of lime (formed in the "black ash" process) on the sodium carbonate (see § 351).

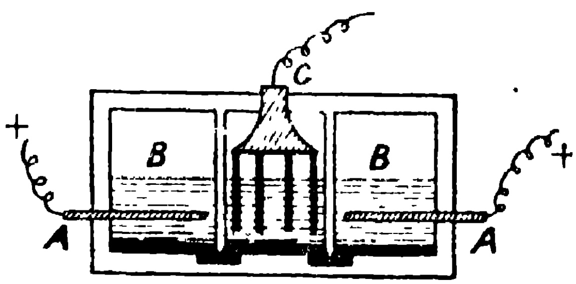

FIG. 81.

340. **Properties of Sodium Hydroxide.**—Sodium hydroxide is a white deliquescent solid with a fibrous structure, and is usually found in the laboratory in the form of sticks some 10 cm. long (formed by using stick-moulds in its manufacture). It dissolves in water with extreme readiness and considerable rise in temperature, forming a strongly alkaline solution. Both the solid and its aqueous solution absorb carbon dioxide very rapidly. Caustic soda exercises a strongly corrosive action on both animal and vegetable tissues.

341. **Sodium Chloride or Common Salt, NaCl.**—This is by far the most important material as a source of sodium salts. In some cases it is obtained in the solid state from mines, but more usually it is brought to the surface in the form of brine and the salt recovered from this by evaporation in pans. On the Continent, in the case of weak brines it is customary to subject the liquor to a preliminary concentration by allowing it to pass over stacks of twigs or brushwood. In England much of the salt is raised as brine, and some idea may be formed of the extensive use which is made of it, from the fact that over two million

tons of salt are produced annually, three-fourths of this in Cheshire, and the rest chiefly in Worcestershire and Durham.

Common salt is used as a glaze for earthenware and for culinary purposes; also as the means of producing "salt-cake" (sodium sulphate), washing soda and "soda ash" (sodium carbonate), and caustic soda, etc. Under ordinary circumstances it separates out on evaporation in the anhydrous condition, but below – 2° C. it is obtained as $NaCl.2H_2O$.

Preparation of Pure Sodium Chloride.—The preparation of pure substances is often a matter of extreme importance to the chemist. The following is a convenient method by which sodium chloride may be obtained very pure.

Exp. 196.—Prepare a saturated solution of common salt, and pass into it a stream of hydrochloric acid gas, previously washed by being allowed to bubble through a bottle containing a small quantity of water. Crystals of NaCl will soon begin to fall out of solution. When a sufficient quantity have collected they may be filtered by suction, washed with a little pure strong HCl, finally with a little absolute alcohol, and then should be left to dry in a desiccator over H_2SO_4, or heated in a steam oven, and allowed to cool afterwards in a desiccator.

The method of purification adopted in the preceding experiment depends upon the insolubility of sodium chloride in a strong solution of hydrochloric acid; small quantities of impurities, such as magnesium chloride, remain in solution.

342. **Sodium Hypochlorite, NaClO,** was formerly an important bleaching agent; like other hypochlorites, it evolves chlorine on treatment with dilute acids. It is obtained by the action of chlorine on dilute caustic soda—

$$Cl_2 + 2\,NaOH = NaCl + NaClO + H_2O.$$

If the solution be hot and strong, and the chlorine in excess, sodium chlorate will be the main product. Sodium hypochlorite has recently been obtained in the solid state in the form of impure crystals.

343. **Sulphites of Sodium.**—*Sodium hydrogen sulphite,* $NaHSO_3$, is prepared in solution by passing sulphur dioxide to saturation into caustic soda or sodium carbonate (carbon dioxide being expelled in this case). An apple-green liquid results from which crystals of the salt are obtained with difficulty by allowing the solution to evaporate *at ordinary temperature.*

If a quantity of caustic soda or sodium carbonate equal to that originally used in preparing the acid salt be added, normal *sodium-sulphite,* Na_2SO_3 is obtained.

These salts when exposed to the air take up oxygen slowly and become converted into the corresponding sulphates—

$$2\ NaHSO_3 + O_2 = 2\ NaHSO_4.$$
$$2\ Na_2SO_3 + O_2 = 2\ Na_2SO_4.$$

Their readiness to pass into sulphates explains the fact that they are both powerful reducing agents.

Thus they absorb chlorine, and the normal salt is on this account used to remove traces of chlorine from articles which have been treated with bleaching powder; hence it is termed an *antichlor.*

$$NaHSO_3 + Cl_2 + H_2O = NaHSO_4 + 2\ HCl.$$
$$Na_2SO_3 + Cl_2 + H_2O = Na_2SO_4 + 2\ HCl.$$

Further, the normal sulphite dissolves sulphur readily with formation of sodium thio-sulphate, $Na_2S_2O_3$, and also the silver salts of the halogen acids.

344. **Sodium Sulphate, Na_2SO_4.**—This salt is obtained in many chemical manufactures, such as those of hydrochloric and nitric acids. It is known commercially as "salt-cake." The hydrated salt, $Na_2SO_4.10\ H_2O$, is known as Glauber's salt. It crystallises in colourless transparent prisms, which melt at 33° C. with decomposition into the anhydrous salt and water.

The solubility curve of sodium sulphate (Fig. 82) is very interesting. It will be seen that there is an abrupt change in the direction of the curve at the point B, which corresponds to a temperature of 33° C. Now this is the temperature at which the hydrated salt loses water as mentioned above, and the explanation of the change in direction of the curve is that the portion A B represents the solubility of the hydrated salt, and the portion B C that of the anhydrous salt. The dotted continuation of the curve C B shows that at temperatures below 33° C. the anhydrous salt is more soluble than the hydrated salt. This can be proved by adding the former to a saturated solution of the latter, below 33° C. The solution dissolves some of the solid, although it is already saturated with the hydrated salt.

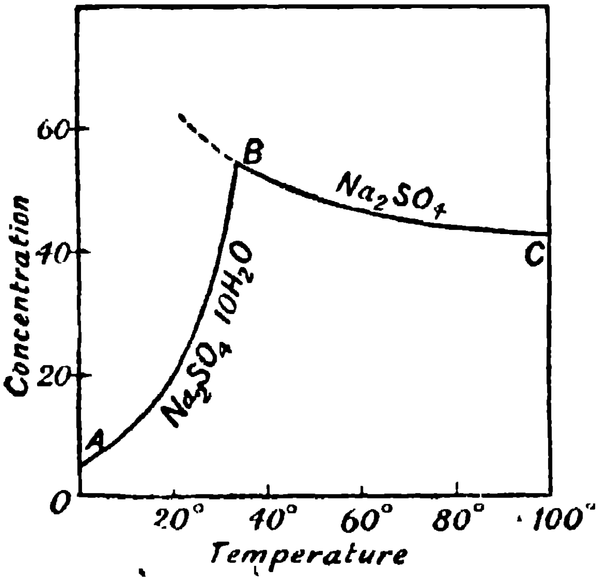

FIG. 82.

Acid sodium sulphate, $NaHSO_4$, is obtained when strong sulphuric acid acts on salt (or sodium nitrate), at a comparatively low temperature, as when the substances are heated in a glass retort. The change which takes place is represented by the equation

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The salt may also be obtained by mixing equivalent solutions of the normal sulphate and sulphuric acid, and crystallising :—

$$Na_2SO_4 + H_2SO_4 = 2\,NaHSO_4.$$

The acid sulphate is much less soluble in water than the normal salt.

345. Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$, is the salt known to photographers as *hyposulphite of soda*. It may be obtained as mentioned above by direct combination of sulphur with sodium sulphite.

Preparation of Sodium Thiosulphate.—

Exp. 197.—Dissolve some crystallised sodium sulphite almost to saturation, in water, in a beaker; stir in flowers of sulphur till some remains undissolved, even on heating. Filter off the excess of sulphur and collect the crystals that form on allowing the filtrate to cool. Pour off the still liquid portion and dry the crystals by pressing them between filter paper.

It is made commercially by the action of Na_2CO_3 on CaS_2O_3, the latter being formed by exposure to air of the tank-waste of the Leblanc process (*q.v.*). Sodium thiosulphate is permanent in air, but aqueous solutions slowly decompose with formation of sodium sulphate and separation of sulphur. On treatment with dilute acids, $Na_2S_2O_3$ evolves SO_2, and gives a white precipitate of finely-divided sulphur—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + SO_2 + S + H_2O.$$

Its use in "fixing" photographic plates depends on its power of dissolving the unaltered portions of the silver compound on the plate. The action in the case of silver chloride (for example), is expressed by the equation

$$Na_2S_2O_8 + AgCl = Na\,Ag\,S_2O_3 + NaCl.$$

Sodium thiosulphate, like sodium sulphite, readily takes up chlorine, and it is therefore employed as an antichlor, its action being expressed by the following equation:—

$$Na_2S_2O_3 + Cl_2 + H_2O = Na_2SO_4 + 2\,HCl + S_2.$$

Iodine also reacts with sodium thiosulphate, but in a different way, as shown in the equation

$$2\,Na_2S_2O_3 + I_2 = \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2\,NaI.$$

This reaction is a quantitative one and is much employed in volumetric analyses.

The uses of $Na_2S_2O_3$ in photography, as an antichlor in bleaching, and as a reagent in volumetric analysis, make it one of the most important of sodium compounds.

346. **Sodium Nitrate or Chili Saltpetre, $NaNO_3$,** is found in the almost rainless districts of Chili, Peru, and Bolivia. It is very soluble in water, from which it crystallises as the anhydrous salt in obtuse rhombohedra almost like cubes (hence the name "cubic nitre"). It is largely used as a manure and also in the manufacture of H_2SO_4, HNO_3, and KNO_3. It cannot be substituted for potassium nitrate in gunpowder owing to its hygroscopic nature.

347. **Phosphates of Sodium.**—Phosphoric acid being tribasic, there are three sodium phosphates, viz. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4. Ordinary commercial sodium phosphate is the second of these compounds. It crystallises in transparent prisms with 12 molecules of water, and is obtained by adding sodium carbonate to phosphoric acid till the solution is just alkaline, and then evaporating. The two other phosphates of sodium are obtained by adding phosphoric acid or caustic soda to the ordinary phosphate—

$$Na_2HPO_4 + H_3PO_4 = 2\,NaH_2PO_4$$
$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O.$$

Of the three phosphates the normal salt, Na_3PO_4, is strong alkaline in solution, the ordinary phosphate is slightly alkaline, whilst NaH_2PO_4 has a distinctly acid reaction. It is frequently found that the normal salts of strong bases with weak acids are alkaline. It is probable that water in such cases decomposes the salt into its constituent base and acid; hence, since caustic soda is dissociated in solution to a far greater extent than phosphoric acid, there are more hydroxyl ions than hydrogen ions present, so that the solution is alkaline.

The dihydrogen salt is converted by heat into the metaphosphate and the monohydrogen salt into the pyrophosphate.

$$NaH_2PO_4 = NaPO_3 + H_2O$$
$$Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Sodium Ammonium Hydrogen Phosphate, or Microcosmic Salt, $NaH(NH_4)PO_4.4\,H_2O$, is obtained by the double decomposition of sodium phosphate with ammonium chloride.

$$Na_2HPO_4 + NH_4Cl = NaCl + NaH(NH_4)PO_4.$$

Preparation of Microcosmic Salt.—

Exp. 198.—Dissolve 36 grammes of the common sodium phosphate, $Na_2HPO_4.12H_2O$, in as small a quantity of hot water as possible, and add 6 grammes of ammonium chloride dissolved in a small volume of water. On cooling, crystals of microcosmic salt fall out of solution. These should be filtered off, washed with a little cold water, and dried between several folds of filter paper.

Heat a small quantity of the crystals in a dry tube till the residue is fused and glassy. Test the evolved gas for ammonia, and the residue for $NaPO_3$. This dissolved in water will give a white precipitate with $AgNO_3$ if the decomposition has been complete.

This salt, like dihydrogen sodium phosphate, is converted into sodium metaphosphate on heating—

$$NaHNH_4PO_4 = NaPO_3 + H_2O + NH_3.$$

348. **Silicates of Sodium.**—A strong solution of sodium silicate, known as water-glass, is used for coating the surface of stone; it is also employed in the manufacture of certain forms of soap, in calico printing, wool cleansing, etc. It is prepared by fusing sodium carbonate with sand or by heating sand with caustic soda under pressure.

349. **Sodium Pyroborate, Borax, $Na_2B_4O_7.10H_2O$,** occurs as a deposit on the site of dried-up inland lakes in some parts of India, in Tibet, and in California. It is extracted by simply boiling with water until a concentrated solution is obtained, and then after settling it is allowed to crystallise out. The boric acid from the lagoons of Tuscany also furnishes it by digestion with soda-ash. It crystallises in monoclinic prisms and is very much more soluble in hot water than cold; 100 parts of water dissolve about five parts of borax at ordinary temperatures and about 200 parts at 100° C.

When heated it is transformed into a soft spongy mass consisting of the anhydrous salt which is used in welding iron. Prolonged heating converts borax into a transparent glassy mass, *borax glass* or anhydrous borax, which has the property of dissolving many metallic oxides, some of which, such as those of iron, manganese, cobalt, etc., yield coloured glasses which serve for the detection of the metals. Borax finds many applications in the arts, and on account of its powerful antiseptic properties it is also employed for preserving articles of food.

The solution of borax in water is quite distinctly alkaline, sufficiently so in fact to allow of the substance being used as a weak alkali for some purposes. The alkalinity of the solution is explained on the same lines as that of a solution of sodium phosphate (§ 347), boric acid being a very weak acid.

350. **Sodium Carbonate, Na_2CO_3,** was formerly obtained by burning seaweed and extracting the ash with water. In this crude form it was known as *barilla*. It is now prepared from salt on a very large scale by (1) the Leblanc process, (2) the ammonia-soda process, or (3) indirectly from caustic soda, the latter being obtained by the electrolysis of brine.

351. **The Leblanc Process.**—Salt is converted first into salt-cake, Na_2SO_4, by the action of sulphuric acid. This is done in two stages, the first being carried out at a gentle heat in a shallow cast-iron pan (see Fig. 83), the reaction being—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The charge is then raked out of the pan and exposed to a stronger heat on the bed of a reverberatory* furnace, when further action takes place as expressed in the equation

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

It would thus appear that half the hydrochloric acid is given off during the treatment in the pan (called "pan-gas") and half during roasting on the bed of the furnace (called "roaster-gas"), though these equations do not accurately represent the stages as they occur in practice, for a larger proportion of the gas is evolved in the former process. The hydrochloric acid gas is cooled and condensed by being passed first through a series of pipes and ultimately through towers packed with coke over which a continual stream of water is kept flowing.

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* *I.e.* a furnace with a roof which deflects the flames from the fire down on to the materials on the bed of the furnace.

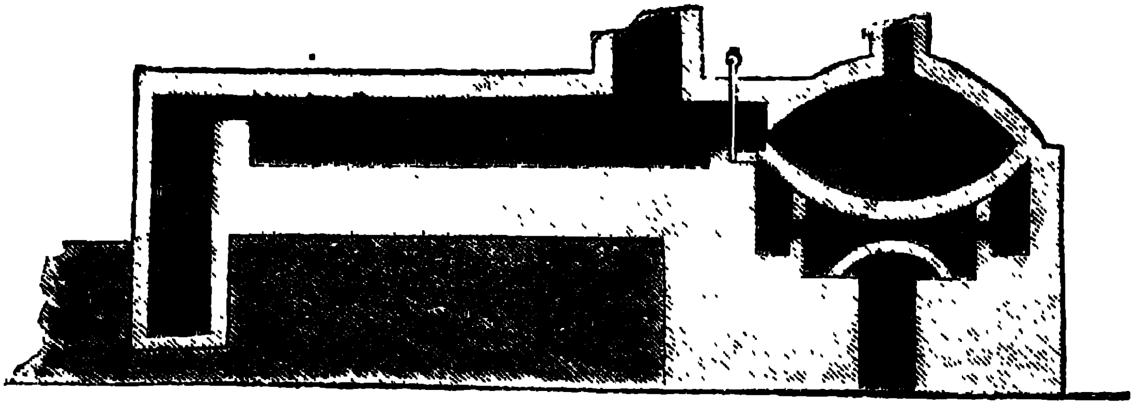

FIG. 83.

Sodium sulphate in a very pure form is also prepared by the Hargreaves process. This consists in bringing sulphur dioxide (prepared from iron pyrites), air, and steam into intimate contact with common salt at about 500° C. The reaction which ensues may be represented by the equation

$$4\ NaCl + 2\ SO_2 + O_2 + 2H_2O = 2\ Na_2SO_4 + 4\ HCl.$$

The salt-cake produced by either of the above processes is then converted into "black ash." It is mixed with the requisite quantities of coal and limestone or chalk and introduced into a "revolver" furnace. This consists of a long cylinder lined with fire-brick, through which the flames from an external fire are passed. The furnace is revolved slowly on its axis during the operation; this brings about a thorough mixing of the charge, and continually exposes a fresh surface to the flames. The principal change which takes place is represented by the equation

$$Na_2SO_4 + CaCO_3 + 2\ C = Na_2CO_3 + CaS + 2\ CO_2.$$

Towards the end of the reaction, carbon monoxide is given off owing to the interaction between the excess of limestone and coal used—

$$CaCO_3 + C = CaO + 2\,CO.$$

When the reaction is complete, the molten mass is poured out through a door into trucks and allowed to cool, forming blocks of *black ash* (so called from the colour).

The black ash is next broken up and lixiviated (*i.e.* digested with water) to dissolve out the sodium carbonate, forming "tank liquor"; a bulky residue called "tank waste" or "alkali waste" is left. The process of lixiviation is rendered as economical as possible by arranging the operation in such a way that the fresh water is pumped upon the nearly exhausted ash; as the solution gradually becomes more saturated it is pumped successively upon less and less exhausted ash until it reaches the saturation point.

The saturated liquor, after settling, is run into shallow pans and evaporated by means of the hot waste gases from the revolver furnaces which are caused to pass over its surface. Crude sodium carbonate separates out, and the crystals are drawn on to drainers placed at the front of the pans. In this way the impure monohydrated carbonate, $Na_2CO_3{\cdot}H_2O$, is obtained,* whilst any caustic soda and most of the other impurities remain in the mother liquor. The crystals are now calcined in a reverberatory furnace to get rid of the water of crystallisation and also to burn off organic matter and transform as much as possible of the impurities (such as sulphide and hydroxide) into carbonate, known in commerce as *soda ash.*

In order to convert soda ash (Na_2CO_3) into crystals of washing soda ($Na_2CO_3,10H_2O$) it is dissolved in water and the solution evaporated and allowed to cool.

352. The Ammonia-Soda Process.—By this process common salt is converted *directly* into sodium bicarbonate. It consists essentially in passing carbon dioxide through an ammoniacal solution of common salt, when the reaction takes the form

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* This salt separates out if the temperature of the solution is above 35° C. (see § 353).

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

Brine is first almost saturated with ammonia and is then run through the pipe A down a tower built of sheet-iron of the construction shown (Fig. 84). The tower is 6 ft. in diameter and at least 50 ft. high; at intervals of about 3 ft. there are compound diaphragms made up of a horizontal flat plate with a large hole in the centre, and over this a curved plate perforated with small holes and deeply cut into grooves round the circumference, as shown in Figs. 85 and 86.

The carbon dioxide is forced in under pressure at the base of the tower at B, and as it rises upwards it meets at the perforations the thin layer of brine which spreads itself over the sieve-like plates. The sodium bicarbonate which forms is carried down through the slits at the edge of the diaphragm. It collects at the base of the tower C, forming a fluid of creamy consistency, and this is periodically drawn off at D, and the salt is separated from it by filtration. The carbon dioxide carries forward with it a certain amount of ammonia, which is recovered by washing the gas after it leaves the upper part of the tower by the pipe E; in order to reduce the quantity of ammonia carried off in this way it is usual to introduce the brine at about the middle of the tower.

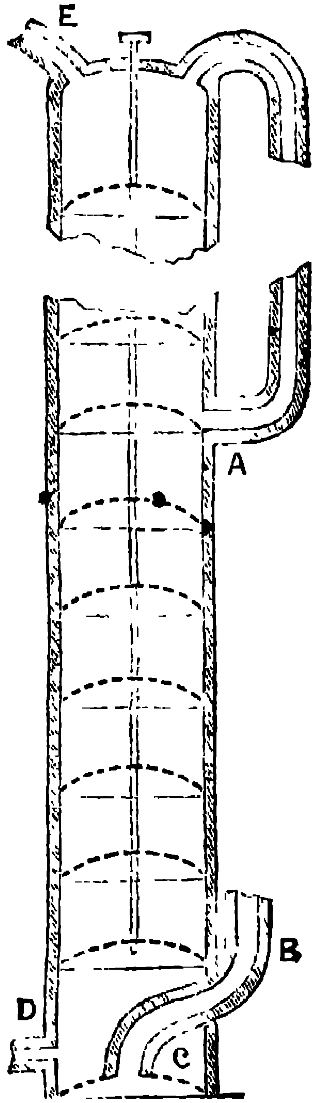

FIG. 84.

The bicarbonate is heated in order to transform it into carbonate—

$$2\,NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

and the CO_2 used in the process is obtained partly in this way, but chiefly (mixed with nitrogen) from lime-kilns.

It will be noticed that ammonium chloride (also ammonium carbonate) is formed and remains in the liquors. The ammonia alone is recovered from this by

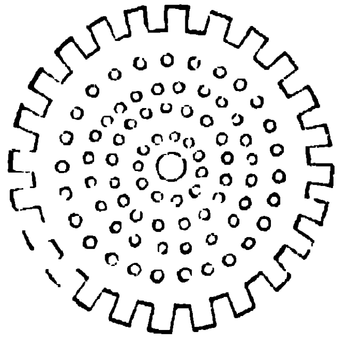

FIG. 85.

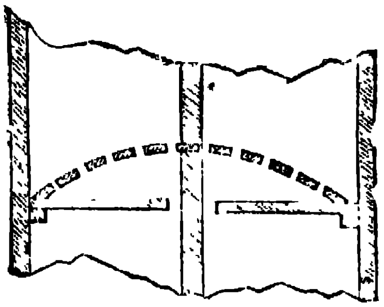

FIG. 86.

heating it along with milk of lime in a specially constructed still—

$$2\,NH_4Cl + CaO = CaCl_2 + 2\,NH_3 + H_2O.$$
$$(NH_4)_2CO_3 + CaO = CaCO + 2\,NH_3 + H_2O.$$

The whole of the chlorine contained in the sodium chloride is lost and passes away in the waste liquors as calcium chloride, but this loss is compensated by the purity of the resulting sodium carbonate, and by the economy in this process as compared with that of Leblanc, in which the carbonate is made by a much more complicated method.

It must be pointed out that the reaction by which sodium bicarbonate is formed in the Ammonia-soda process is a reversible one, *i.e.* sodium bicarbonate and ammonium chloride react under suitable conditions to form sodium chloride and ammonium bicarbonate.

$$NaHCO_3 + NH_4Cl = NaCl + NH_4HCO_3.$$

This is the reverse of the action

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

We may consider that the reaction given above between common salt, ammonia, carbon dioxide, and water takes place in two stages, of which the first is

$$NH_3 + CO_2 + H_2O = NH_4HCO_3,$$

and the second the reaction just given.

Now the reaction in which sodium bicarbonate is formed requires a low temperature, the reverse change taking place if the temperature rises too high. Hence in practice the temperature is kept low by the following procedure.

(*a*) During the solution of the NH_3 in the brine, the liquid is cooled by cold water running through a worm contained in the absorption apparatus.

(*b*) The liquid is subsequently cooled before being sent into the carbonating tower.

(*c*) The carbonating tower itself is cooled by running cold water over the outside whilst it is working.

353. **Commercial Forms of Sodium Carbonate.**—Sodium carbonate comes into the market in three forms:—(1) *Carbonate of soda,* or *soda-ash,* Na_2CO_3; (2) *crystal carbonate,* $Na_2CO_3 . H_2O$; and (3) *soda crystals* or *washing soda,* $Na_2CO_3 . 10\ H_2O$.

Properties of Sodium Carbonate.—Anhydrous sodium carbonate is a white powder which melts on strongly heating and solidifies again to a white porous mass. It dissolves readily in water with rise in temperature and formation of an alkaline solution.

From this solution three different hydrated salts separate out according to the temperature, as indicated below:—

Above 35° C.,	$Na_2CO_3 . H_2O$.
Between 32° and 35° C.,	$Na_2CO_3 .\ 7\ H_2O$.
Below 32° C.,	$Na_2CO_3 .\ 10\ H_2O$.

The decahydrated salt, common washing soda, forms large transparent crystals which effloresce in dry air falling to a powder consisting of the monohydrated salt. When the crystals are gently heated they melt in their water of crystallisation, and then lose water, being converted into the monohydrate; the remaining molecule of water is lost at a temperature slightly above the boiling point of water.

354. **Hydrogen Sodium Carbonate,** or sodium bicarbonate, is obtained on the large scale by the ammonia-soda process above described. It is also formed by the action of carbon dioxide on the normal carbonate, either crystalline or in solution—

$$Na_2CO_3 + H_2O + CO_2 = 2\ NaHCO_3.$$

$NaHCO_3$ is a white powder, much less soluble in water than the normal carbonate. On heating the solid bicarbonate, or on prolonged boiling of its solution, the above reaction is reversed, the normal carbonate being formed again.

QUESTIONS.—CHAPTER XXVI.

1. Describe the method by which Davy obtained sodium and the modifications which have since been introduced in the method so as to render it suitable for the preparation of the metal on the large scale.
2. Describe the preparation of pure sodium peroxide. How is it made on the large scale? What experiments would you perform to obtain from this substance (*a*) oxygen, (*b*) hydrogen peroxide? Explain its use in the analysis of minerals such as chrome ironstone, and as a bleaching agent.
3. How would you prepare specimens of pure caustic soda and pure sodium chloride respectively? How can both these substances be converted into sodium arbonate and bicarbonate respectively?
4. Describe the methods of theoretical and practical importance by which sodium sulphate is obtained. Indicate the steps by which this substance is converted by the Leblanc process into sodium carbonate.
5. What is the nature of the substance obtained by boiling sodium sulphite solution with sulphur? How would you prepare a fairly pure specimen of the substance? Describe the behaviour of the substance towards air, water, and acids.

6. Explain the use of sodium thiosulphate (*a*) as an antichlor, (*b*) as a reagent in volumetric analysis, (*c*) in photography.
7. What is the formula for microcosmic salt? How would you prepare a specimen of this body? Describe the effect of heat upon the substance.
8. What is borax? How is it usually prepared? What happens when it is heated? How do you explain the alkalinity of a solution of borax?

CHAPTER XXVII.

POTASSIUM AND AMMONIUM.

POTASSIUM.

355. **Occurrence.**—Potash occurs in combination chiefly with alumina and silica in the older rocks as potash felspar (orthoclase) $K_2O.Al_2O_3.6SiO_2$, potash mica (muscovite) $(KH_2)Al_3(SiO_4)_3$, and in other mineral silicates. It is also found locally in the neighbourhood of Stassfurt as Carnallite, $KCl.MgCl_2.6\ H_2O$, in East Galicia as Sylvine, KCl, and as nitrate in the form of an efflorescence on the soil in the rainless districts of Peru, Chili, etc.

The ash of plants contains a notable quantity of potassium salts, chiefly carbonate, which may be extracted by water. Almost the whole of the potash salts used to be obtained in this way, and from the fact of their being extracted by boiling their ash in pots the salts were termed "Pot-ashes" (hence *potash*), a more refined product being called "pearl-ash."

In more recent times the residues from the manufacture of beetroot sugar have been employed as a source of potassium salts, the liquors being evaporated and calcined; a product is thus obtained which contains about 60 per cent. of potassium salts. The washings of sheep's wool ("suint") by similar treatment yield a residue containing about 90 per cent. of potassium salts. The ashes from "kelp" were formerly largely extracted, but now are employed to a smaller extent, and only crude salts are prepared from them. By far the most important source of potassium salts is the mines at Stassfurt, where over 100,000 tons of the chloride are annually produced.

356. **Metal.**—This was first obtained by Davy in 1807 by the electrolytic decomposition of fused caustic potash (see § 334). It was afterwards prepared on a larger scale by Gay Lussac and Thénard by strongly heating caustic potash in contact with metallic iron.

One method in use at the present time for the manufacture of potassium consists in heating an intimate mixture of potassium carbonate and carbon (obtained by igniting crude potassium tartrate in a closed vessel) in cylindrical iron retorts placed horizontally, as shown in Fig. 87. The principal reaction is

$$K_2CO_3 + 2\,C = 2\,K + 3\,CO.$$

The carbon monoxide and vapours of potassium pass off by the tube into a receiver which presents a large area for cooling. The receiver, as shown in the figure, is made up of two flat plates screwed together so as to leave a narrow space between them, and the potassium condenses between these and is periodically removed and preserved in petroleum.

This method never gives anything near the theoretical yield of potassium, and it is accompanied by the formation of a black explosive carbonyl compound $K_6C_6O_6$, which renders the manufacture dangerous. The object of the special flat condenser shown above is to cool the potassium as rapidly as possible, as this diminishes, though it does not entirely prevent, the formation of the explosive compound.

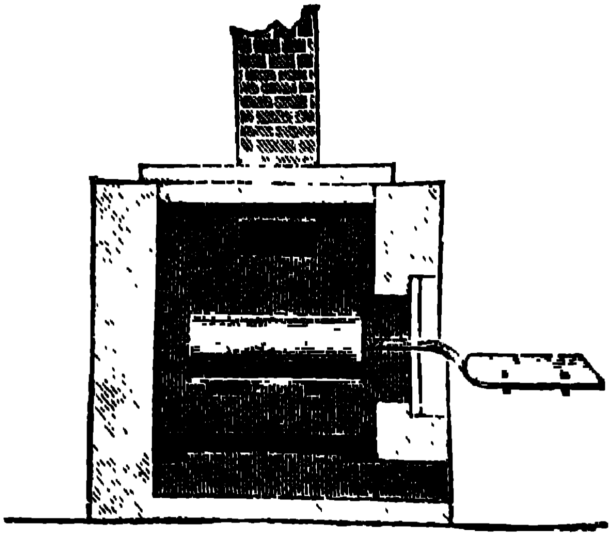

FIG. 87.

Another method now employed for the manufacture of potassium consists in the electrolysis of fused potassium chloride.

Properties.—Potassium is a soft metal with a silvery lustre; it has a sp. gr. of 0·875, and is lighter than sodium; it melts at 62° C. and boils at a dull red heat, forming a green vapour, whose density is 19. Though not acted upon by perfectly dry oxygen it rapidly tarnishes by oxidation in moist air even at ordinary temperatures. It likewise combines directly with hydrogen and the halogens and with sulphur, selenium, and phosphorus when heated. It decomposes water at ordinary temperatures according to the equation

$$2\,K + 2\,H_2O = 2\,KOH + H_2,$$

and almost all oxides undergo a partial or complete reduction if they are heated in contact with potassium. K and Na in the proportions 2 K : Na form an alloy which is liquid at ordinary temperatures.

357. **Potassium hydride, KH.**—This substance has, like the corresponding sodium compound, been recently prepared by Moissan. Pure dry hydrogen is passed over potassium heated to 360°. The hydride consists of slender white acicular needles; it is insoluble in benzene, ether, and carbon bisulphide, but is readily decomposed by atmospheric air and by water.

358. **Oxides of Potassium.—Potassium Monoxide, K_2O.**—This oxide, like the corresponding sodium compound, has recently been prepared by heating potassium with potassium nitrate in the proportions required by the equation

$$2\,KNO_3 + 10\,K = 6\,K_2O + N_2.$$

It is a greyish non-lustrous solid which forms potassium hydroxide when added to water.

Potassium Tetroxide.—By gradual heating of potassium in air or oxygen it passes into a chrome yellow powder consisting of the *tetroxide*, K_2O_4. This oxide is a powerful oxidising agent, and when heated in carbon monoxide oxidises it and forms potassium carbonate, oxygen being also given off—

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

359. **The Hydroxide** is obtained (1) when water is acted upon by metallic potassium, or (2) when a solution of potassium carbonate is boiled with milk of lime—

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + 2\,KOH.$$

The boiling is continued till a sample of the supernatant liquid, after settling, no longer effervesces when dilute acid is added to it. The calcium carbonate is then settled out and the clear liquid decanted off and boiled down to expel water until it is found to solidify on cooling. It usually contains as impurities, alumina, silica, and carbonates of calcium and potassium; these are all insoluble in alcohol, whilst potash is freely soluble. By shaking up the potash with alcohol the impurities are left undissolved, and can be allowed to settle; if the clear solution is boiled down in a silver basin, pure potash is left behind.

Exp. 199.—Prepare pure caustic potash from potassium carbonate as just described.

Caustic potash may also be obtained by the double decomposition of the sulphate with barium hydroxide—

$$K_2SO_4 + Ba(OH)_2 = 2\,KOH + BaSO_4.$$

The barium sulphate is an insoluble heavy powder which may be readily settled out.

Caustic potash is, as its name implies, strongly caustic and acts very powerfully on animal and vegetable tissue; when exposed to air it readily takes up carbon dioxide, forming the carbonate. Other gases, as for instance SO_2, Cl_2, and H_2S, are also taken up by it, so that it is often of service for the removal of such gases when they occur as impurities. It is one of the most active bases, and from it most of the salts of potassium may be prepared by the addition of an equivalent amount of the corresponding acid.

360. **Potassium Chloride, KCl,** is formed by direct union of its elements, or by neutralising caustic potash by means of hydrochloric acid. Like sodium chloride, it crystallises in the anhydrous condition in cubes. It is less soluble

than sodium chloride at low temperatures and much more soluble at higher temperatures, as shown by the solubility curves in Fig. 88. Hence, if a saturated solution containing both chlorides is gradually cooled down, it is chiefly potassium chloride which crystallises out, and in this way the two chlorides are separated from one another on the large scale.

A little sodium chloride will separate out along with the potassium chloride, but this may be removed by redissolving the salt in hot water and allowing the solution to crystallise. The potassium chloride will now separate out while the sodium salt remains dissolved, because there is not sufficient of it present to saturate the solution. This illustrates the process of *fractional crystallisation* which is very frequently utilised for the purification of salts.

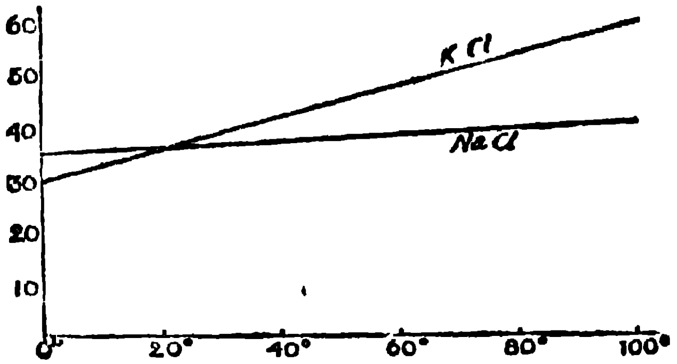

FIG. 88.

361. **Potassium Bromide, KBr,** is more readily soluble in water than the chloride; it may be obtained by adding hydrobromic acid to the hydroxide or carbonate, or better by mixing together warm solutions of potassium carbonate and bromide of iron, obtained by adding bromine to moistened iron filings. The following are the reactions:—

(1) $Fe+Br_2=FeBr_2$.

(2) $3\,FeBr_2+Br_2=Fe_3Br_8$ (ferroso-ferric bromide).

(3) $Fe_3Br_8+4\,K_2CO_3+4\,H_2O=Fe_3(OH)_8+8\,KBr+4\,CO_2$.

The hydroxide of iron being insoluble can be separated by filtration. The solution on evaporation and cooling deposits cubic crystals of potassium bromide.

362. Potassium Iodide, KI, is obtained by similar methods to those employed for the bromide; on the large scale a method similar to the last of these is employed, iodine being used in place of bromine. Potassium iodide may also be obtained by the action of iodine on caustic potash—

$$3\ I_2 + 6\ KOH = 5\ KI + KIO_3 + 3\ H_2O.$$

At a red heat the iodate is reduced by carbon—

$$KIO_3 + 3\ C = KI + 3\ CO.$$

It is also decomposed on heating alone, but a higher temperature is required—

$$2\ KIO_3 = 2\ KI + 3\ O_2.$$

Exp. 200.—Take about 50 c.c. of strong caustic potash and add iodine to it gradually till the liquid acquires a permanent yellow colour (*i.e.* the KOH has dissolved as much iodine as it can take up). Evaporate the liquid to dryness and transfer the residue (a mixture of KI and KIO_3) to a hard glass tube. Heat strongly and prove that oxygen is evolved. When the evolution of oxygen ceases allow the residue to cool, dissolve it in water and crystallise out the potassium iodide.

This salt can be vaporised without decomposition; a determination of its vapour density at a bright red heat gave a value corresponding to the formula KI. Potassium iodide is freely soluble in water and in alcohol, and its solutions dissolve iodine. At 20° C., 100 pts. of water dissolve 35, 65, and 144 pts. of KCl, KBr, and KI respectively. These three salts exhibit a similar gradation of properties in their melting points and densities. They all crystallise in cubes.

Chlorine water sets free the halogen element from bromide and iodide of potassium—

$$3\ KI + Cl_2 = 2\ KCl + I_2.$$

If a concentrated solution of potassium iodide be saturated with iodine and left over sulphuric acid, dark blue needles of the triiodide KI_3 separate out.

363. **Potassium Hypochlorite, $KClO$,** is only known in solution; it is prepared by acting on a solution of caustic potash with chlorine *in the cold*—

$$2\ KOH + Cl_2 = KClO + KCl + H_2O.$$

Potassium hypochlorite, like the sodium salt, was formerly used as a bleaching agent on account of the readiness with which it gives up chlorine on treatment with dilute acids—

$$KClO + 2\ HCl = KCl + H_2O + Cl_2.$$

Potassium and sodium hypochlorites constitute useful oxidising agents, since they readily give up oxygen to many substances in alkaline solution. Litharge (PbO), for example, is converted into lead dioxide (PbO_2) by either of these salts—

$$PbO + NaOCl = PbO_2 + NaCl.$$

364. **Potassium Chlorate, $KClO_3$.**—When chlorine is passed into a *hot* solution of caustic potash, potassium chlorate is formed, together with the chloride, according to the equation

$$6\ KOH + 3\ Cl_2 = KClO_3 + 5\ KCl + 3\ H_2O.$$

The employment of so large a quantity of the expensive potassium salt, and the difficulty of recovering it, has led to the adoption of a modification of the method, where potassium chlorate is prepared on the large scale.

This consists in the formation of calcium chlorate by saturating a warm mixture of lime and water with chlorine, the reaction being similar to that with potash—

$$6\ Ca(OH)_2 + 6\ Cl_2 = Ca(ClO_3)_2 + 5\ CaCl_2 + 6\ H_2O.$$

The liquid, after being allowed to settle, is run off and concentrated somewhat by evaporation; potassium chloride in slight excess of the equivalent for $Ca(ClO_3)_2$ is added, and a double decomposition takes place—

$$Ca(ClO_3)_2 + 2\ KCl = 2\ KClO_3 + CaCl_2.$$

The potassium chlorate is much less soluble than the calcium chloride, so that, on further concentration and careful cooling, crystals of potassium chlorate separate. This is then purified by recrystallisation.

Exp. 201.—Prepare crystals of pure potassium chlorate starting with milk of lime and using the method just described. Test the purity of your specimen by adding $AgNO_3$ to an aqueous solution. If the $KClO_3$ is quite pure there should be no precipitate, showing the absence of chlorides.

Potassium chlorate is used for the preparation of oxygen, and is, in presence of mineral acids, a powerful oxidising agent; it is also largely employed in the manufacture of matches and in pyrotechny.

365. **Potassium Perchlorate, $KClO_4$.**—This is the most stable of the series of potassium salts derived from the oxy-acids of chlorine. It is obtained (with chloride) by heating potassium chlorate until the salt becomes pasty.

$$4\ KClO_3 = 3\ KClO_4 + KCl.$$

Any chlorate which remains may be decomposed by warming with concentrated hydrochloric acid, which is without action on the perchlorate; the chloride is much more soluble in water than the perchlorate, so that the latter may be readily separated by crystallisation.

366. **Potassium Sulphate, K_2SO_4,** is found in the neighbourhood of Stassfurt in the mineral kainite, $K_2SO_4.MgSO_4.MgCl_2.\ 6\ H_2O$, from which it can be obtained by fractional crystallisation. Magnesium chloride remains in the mother liquors, and a hot saturated solution of the crystals, $K_2SO_4.MgSO_4.\ 6\ H_2O$, which separate, is digested with solid potassium chloride, when the following reaction takes place:—

$$K_2SO_4.MgSO_4 + 3\ KCl = 2\ K_2SO_4 + KCl.MgCl_2.$$

The potassium sulphate crystallises much more readily than the potassium magnesium chloride, and may thus be easily separated from the liquid.

Potassium sulphate is also made by the action of sulphuric acid on the chloride, after a manner similar to that employed on the larger scale for sodium sulphate; it is chiefly used in agriculture.

Potassium Hydrogen Sulphate, $KHSO_4$.—When potassium chloride or nitrate is treated with excess of sulphuric acid until the hydrochloric or nitric acid is volatilised and the liquid is then allowed to cool, crystals of this salt separate out.

Many minerals which withstand the action of acids are brought into a soluble form by fusion with this salt. Thus chrome ironstone, $FeO.Cr_2O_3$, on fusion with $KHSO_4$ yields a mixture of chromium and iron sulphates. The salt behaves, in fact, like sulphuric acid, but a much higher temperature is possible than with H_2SO_4 alone. It is on this account used for the purpose of cleaning platinum crucibles.

367. **Potassium Nitrate, KNO_3,** known also by the familiar names *nitre* or *saltpetre,* is found in the surface soils in India and Persia, where a sufficiency of nitrogenous matter exists, and the climate is sufficiently dry to allow of its accumulation.

It is manufactured by boiling together concentrated solutions of Chili saltpetre ($NaNO_3$) and potassium chloride, when a double decomposition takes place, and sodium chloride, which is much less soluble in *hot water* than nitre, though more soluble in *cold water,* separates out and is removed *in the heat* by canvas filters; potassium nitrate crystallises out from the mother liquor on cooling.

It is obtained also artificially by a method resembling that by which it is formed in the soils of eastern countries. Heaps of ashes and lime are drenched with urine and other nitrogenous refuse; after being exposed to the air for some time the nitrogenous substances become oxidised (by the agency of bacteria), and, on lixiviation, the liquor is found to contain large quantities of nitrates. Treatment with potassium carbonate gives rise to the formation of potassium nitrate, which can be extracted in a crude form by crystallisation after filtering off the precipitated calcium carbonate.

Potassium nitrate is very soluble in water; 100 parts of water at 15° C. dissolve 26 parts of the salt, and at 100° C. about 250 parts.

When strongly heated it gives off oxygen, and is transformed into potassium nitrite, KNO_2, and in presence of charcoal a violent deflagration takes place, the reaction approximating to the equation

$$4\,KNO_3 + 5\,C = 2\,K_2CO_3 + 3\,CO_2 + 2\,N_2.$$

Potassium nitrate is therefore a powerful oxidising agent, organic substances and carbonaceous matter if fused with it being readily decomposed with the formation of potassium carbonate, carbon dioxide, and carbon monoxide.

Sulphur under similar circumstances is oxidised with the formation of potassium sulphate and sulphur dioxide—

$$2\,KNO_3 + 2\,S = K_2SO_4 + SO_2 + N_2.$$

368. **Gunpowder.**—A mixture of potassium nitrate, charcoal, and sulphur finds application as gunpowder, the propelling power of which is due to the fact that the nitrate supplies oxygen by which the combustion of the sulphur and carbon is effected in a closed space. The volume of the gases generated, even when measured at the standard temperature and pressure, amounts to about 380 times that of the space occupied by the gunpowder; as the temperature generated is over 2000° C., it is evident that the volume is very much greater, and the pressure produced has been estimated at over 6000 atmospheres, or about 42 tons on the square inch. The composition of gunpowder varies according to the use to which it is applied; typically it has the proportions agreeing to the formula $2\,KNO_3 + 3\,C + S$, and the percentage composition of some forms of it is given in the following table:—

	KNO_3	C.	S.
$2\,KNO_3 + 3\,C + 1\,S$ =	74·8	13·4	11·8
English military powder =	75·0	15·0	10·0
English sporting powder =	79·7	12·5	7·8
Ordnance powder =	73·8	13·4	12·8

369. **Potassium Carbonate, K_2CO_3,** has been mentioned already as occurring in the incinerated residue from plants. It is also prepared from the sulphate by a method corresponding to the Leblanc process, by which sodium carbonate is obtained (see § 351). By the action of carbon dioxide, the bicarbonate, $KHCO_3$, is obtained. Both salts are freely soluble in water, the former at ordinary temperatures in its own weight of water, and the latter in four times its weight of water. Potassium carbonate withstands high temperatures without decomposition, but the bicarbonate readily loses carbon dioxide and water, and is transformed into the carbonate—

$$2\ KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

Like several other of the salts of potassium derived from weak acids, the normal salt possesses an alkaline reaction.

370. **Potassium Permanganate, $KMnO_4$.**—This salt is best prepared as follows:—A stong solution of caustic potash is added to a mixture of potassium chlorate and manganese dioxide. The mixture is evaporated to dryness and strongly heated, when the following change takes place—

$$3\ MnO_2 + KClO_3 + 6\ KOH = 3\ \underset{\text{Potassium manganate}}{K_2MnO_4} + KCl + 3\ H_2O.$$

The mass of manganate and chloride is then broken up and lixiviated with water, forming a dark green solution. On passing carbon dioxide into this, three-quarters of the manganate is converted into permanganate, the remainder forming a brown precipitate of hydrated sesquioxide—

$$8\ K_2MnO_4 + 5\ CO_2 + H_2O = 6\ KMnO_4 + 5\ K_2CO_3 + Mn_2O_3.H_2O.$$

The precipitate is filtered off and the liquid evaporated and allowed to crystallise.

Potassium permanganate crystals are almost black and have a metallic lustre. They dissolve in about 15 times their weight of water, forming a deep purple solution which is nearly opaque. In acid or neutral solution the permanganate is stable, but in alkaline solution it changes into the manganate, and finally into the dioxide, evolving oxygen.

Potassium permanganate is a powerful oxidising agent. A mixture of the solid with sulphur or carbon or phosphorus explodes violently; and in acid solution the permanganate at once oxidises ferrous to ferric salts, and oxalic acid to carbon dioxide, the manganese being converted into a manganous salt. As $2KMnO_4$ is equivalent to $K_2O.Mn_2O_7$, and since the heptoxide is reduced to MnO the oxide corresponding to a manganous salt, it is clear from the equation

$$Mn_2O_7 = 2\,MnO + 5\,O$$

that two molecules of the permanganate are equivalent to five atoms of oxygen, and will therefore oxidise ten molecules of ferrous salt or five molecules of oxalic acid—

$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$$

$$5\,H_2C_2O_4 + 2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

Potassium permanganate is largely used in volumetric analysis for determining the quantity of a reducing agent, *e.g.* ferrous iron, in a solution, a permanganate solution of known strength being run into the reducing solution from a burette until it ceases to be decolorised.

Exp. 202.—Starting from pyrolusite, prepare a solution of potassium manganate, and then convert this into the permanganate. Acidify some of the permanganate solution with dilute sulphuric acid and note the effect of (*a*) passing a current of sulphuretted hydrogen through the solution, (*b*) adding the solution gradually to (1) sulphurous acid, (2) ferrous sulphate solution, (3) hot oxalic acid solution. Finally warm some $KMnO_4$ with caustic potash and note what takes place.

A crude mixture of sodium manganate and permanganate, obtained on a large scale by heating caustic soda with pyrolusite, is sold as a disinfectant under the name of "Condy's fluid." It owes its value as a disinfectant to its oxidising properties.

AMMONIUM

371. This name is applied to the hypothetical radical NH_4, the salts of this radical being very similar in general character to those of the alkalies. When sodium amalgam is brought into a strong solution of ammonium chloride the amalgam swells up to many times its original bulk and forms a spongy mass owing to the inclusion of a large volume of gas. No sooner is this brought about than ammonia and hydrogen are given off from the mass in such proportions as to point to NH_4 as the source. Of course these are the proportions we should expect, since sodium removes the chlorine from NH_4Cl, leaving NH_4, which then breaks up into NH_3 and hydrogen—

$$Na + NH_4Cl = NaCl + NH_4;\ 2\ NH_4 = 2\ NH_3 + H_2.$$

It has never been established that the NH_4 exists even temporarily in the free state; but it may be pointed out that neither ammonia nor hydrogen has any action at all on mercury, and it is difficult to regard the "amalgam" as a mere sponge of mercury containing the two gases mechanically mixed.

Ammonium salts are invariably obtained by the combination of ammonia with the acid of the salt; thus, neutralising various acids with ammonia, we have—

$$\begin{aligned} 2\ NH_3 + H_2SO_4 &= (NH_4)_2SO_4, \\ NH_3 + HCl &= NH_4Cl, \\ NH_3 + HNO_3 &= NH_4NO_3. \end{aligned}$$

Coal contains between 1 and 2 per cent. of nitrogen, and during its distillation for the production of coal gas some of this is transformed into ammonia, and on washing the coal gas it is dissolved out. Gas liquor consists of these washings and contains considerable quantities of ammonia, mostly as sulphide, but partly in other forms and as free ammonia. By distilling the liquor over lime the ammonia is set free and then "fixed" by passing it into sulphuric acid. The ammonium salts which come into commerce are chiefly obtained from gas liquor, the bulk of the supply being used in the form of ammonium sulphate as a fertilising agent, and a considerable amount as free or caustic ammonia in the ammonia-soda process.

372. **Ammonium Hydroxide, NH_4OH,** exists only in solution at ordinary temperature,* as it decomposes very readily into ammonia and water. That it is a true hydroxide, however, is shown by its basic character and its general resemblance in chemical actions to the caustic alkalies, *e.g.* it precipitates the hydroxides of iron and aluminium from salts of these metals and saponifies fats and oils. Ammonia is, however, a very much weaker base than either caustic potash or caustic soda.

373. **Ammonium Chloride, NH_4Cl.—Dissociation.**—Ammonium chloride is obtained as above or by direct combination of ammonia and hydrochloric acid in the gaseous condition.

When ammonium chloride is heated it *apparently* sublimes unchanged, the vapour condensing again to ammonium chloride, and this method is employed for its purification. It has been shown, however, that the vapour is not that of ammonium chloride, but is a mixture of ammonia and hydrogen chloride, which recombine on cooling—

$$NH_4Cl = NH_3 + HCl.$$

Such a change as this in which a compound splits up on heating into constituents which recombine on cooling is called *dissociation.* That dissociation has taken place in this case is proved by the fact that the density of the vapour is only half what it should be if it consisted of NH_4Cl molecules.

The following argument will make this clear:—Each NH_4Cl molecule gives rise to one NH_3 molecule and one HCl molecule, so that if the pressure remains the same the volume of mixed gases will be double the volume which the undissociated ammonium chloride would occupy

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* Ammonium hydroxide has recently been isolated at low temperature.

(by Avogadro's hypothesis). But since the volume is double, the density must be one-half what it would be if the salt remained undissociated (the *mass remaining the same*).

The dissociation may be proved directly by partially separating the two gases by diffusion.

Exp. 203.—Take a piece of hard glass tube of about 3 cm. bore and 25 cm. long. Fit it with a one-holed cork at each end, through which passes a long piece of clay pipe-stem, which has been made red hot. In the middle of the glass tube place some fragments of the fibrous sal-ammoniac, and at both ends a piece of moist blue litmus paper. Fix in the corks tightly, clamp the tube horizontally, and attach to one of the ends of the pipe-stem a scent bellows (Fig. 89). After warming the tube carefully, place a burner under the sal-ammoniac. When the tube is red hot, blow the bellows and test the gas which comes through the pipe stem with litmus or turmeric paper.

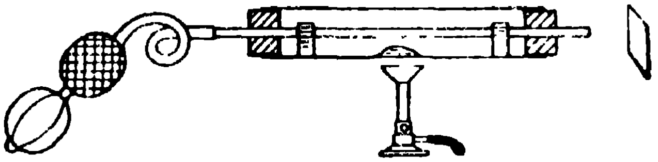

FIG. 89.

It will be noted that the air which passes through the pipe-stem is alkaline from the presence of ammonia, while the vapour which is left in the tube is acid. This can be explained when it is remembered that light gases diffuse much more rapidly through porous substances than heavy ones (§ 54). Ammonia is lighter than hydrogen chloride and therefore diffuses faster, but it could not do so here unless it were free and not combined.

The extremely interesting observation has been made by Baker that ammonium chloride, if thoroughly dried, does not dissociate when vaporised. He employed a Victor Meyer vapour density apparatus modified as shown in Fig. 90, the pure substance being placed at *a* in a spoon which could be inverted by means of the handle *b*. The upper part *c* contained P_4O_{10} to dry the interior of the apparatus. The drying process was allowed to go on for three weeks. The mean of six experiments gave 27·8 as the vapour density, showing that very little dissociation had taken place.

The temperature at which vaporisation was effected was 350° C. It seems therefore from this and similar experiments with other substances, notably mercurous chloride, that dissociation is due in some way to the presence of water-vapour. How the moisture acts is not exactly known.

Ammonium chloride is freely soluble in water and in alcohol. It is used in dyeing and in soldering and tinning; also as a reagent in the laboratory.

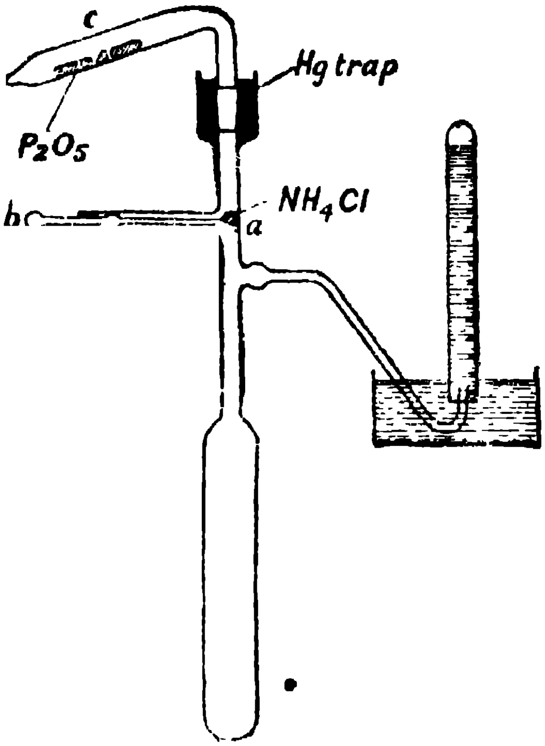

FIG. 90.

374. **Ammonium Nitrate, NH_4NO_3,** is prepared by neutralising nitric acid with ammonia and evaporating the solution until it crystallises on cooling. When heated it breaks up into nitrous oxide and water. (See § 206.) When rapidly heated, as for instance by contact with a red-hot metal, it detonates, as it does also when heated in presence of organic matter, and it is used in the production of certain forms of explosives.

Ammonium Carbonate.—By the direct combination of ammonia and carbon dioxide in presence of moisture, or by subliming an intimate mixture of ammonium sulphate and chalk, there is obtained the commercial carbonate of ammonium, which is, however, essentially a mixture of *ammonium bicarbonate*, NH_4HCO_3, and *ammonium carbamate*, $NH_4.CO_2NH_2$. These compounds are very unstable and undergo slow decomposition even at ordinary temperatures, and this accounts for the ammoniacal odour which is perceived when they are exposed to air.

375. **The Alkali Metals a Natural Group.**—The metals sodium and potassium, together with several rarer metals, closely resemble each other in properties and are classified together as the *alkali metals* (from the fact that they form the basis of the alkalies caustic soda, caustic potash, etc.). *Ammonium*, which, as we have seen, behaves very much like them, is also included in the group.

The following summary of the general characters of the alkali metals brings out clearly the justification for classifying them together:—

(1) The elements are monovalent and replace the hydrogen in acids atom by atom, forming normal and acid salts, *e.g.*—

From HCl, salts of the type RCl.
„ H_2SO_4, „ „ „ R_2SO_4 and $RHSO_4$.
„ H_3PO_4, „ „ „ R_3PO_4, R_2HPO_4, RH_2PO_4
$R = Na$, K or NH_4.

(2) The metals are soft and malleable; they decompose water at the ordinary temperature and form strongly basic hydroxides—

$$2\,R + 2\,H_2O = 2\,ROH + H_2.$$

Also they undergo oxidation when exposed to air at ordinary temperatures.

(3) The normal carbonates are stable at high temperatures (ammonium carbonate is an exception).

(4) The metals combine directly with hydrogen when heated in it, forming *hydrides* of the general composition RH.

(5) These metals exhibit no tendency to form basic salts.

(6) The metals may be obtained—

(*a*) by the electrolysis of the fused hydroxide or chloride,

(*b*) by the action of carbon at high temperature on the hydroxide or carbonate.

$$R_2CO_3 + 2\,C = 2\,R + 3CO.$$

QUESTIONS.—CHAPTER XXVII.

1. Describe the preparation of potassium from potassium carbonate. What are the chief properties of metallic potassium?
2. How would you prepare potassium bromide and potassium iodide (*a*) from potassium carbonate, (*b*) from caustic potash?
3. How is chlorate of potash usually obtained on the large scale? How would you proceed to prepare a specimen of the perchlorate from it?
4. Describe how you would prepare a specimen of pure caustic potash from commercial potassium carbonate. Express by equations the changes which take place when the following gases are respectively passed into a solution of caustic potash:—*Chlorine, sulphur dioxide, sulphuretted hydrogen.*
5. Describe the preparation of potassium permanganate from pyrolusite (manganese dioxide). Give several examples (with equations) of the oxidising action of this salt.
6. With what other element would you classify potassium? Give reasons.
7. What is the chief source of the compounds of ammonia? Describe the preparation of pure ammonium sulphate and ammonium nitrate from this source.
8. How would you prepare a specimen of pure ammonium chloride? What experiments would you perform to demonstrate the chief properties of this substance? What do you know about its vapour density?
9. Describe the effect of heating the following compounds of ammonium: the sulphate, chloride, nitrate, carbonate, and nitrite.

CHAPTER XXVIII.

CALCIUM AND ZINC.

CALCIUM.

376. **Occurrence.**—As *carbonate* (limestone) it is found in rock masses, and also in crystals as calcite and arragonite; as *sulphate* in the forms anhydrite, the anhydrous sulphate, $CaSO_4$, and gypsum, the hydrated form, $CaSO_4.2H_2O$; as *fluoride* in fluorspar, CaF_2, and as *phosphate* in apatite, $3Ca_3P_2O_8.Ca(F,Cl)_2$. Dolomite (or magnesian limestone) is calcium carbonate in which part of the calcium is replaced by magnesium, $(Ca,Mg)CO_3$.

377. **Metal.**—The metal is obtained by heating the anhydrous iodide with sodium, or by electrolysing the fused chloride, preferably mixed with strontium or barium chloride, in order that the fusion may be brought about at a lower temperature.

Calcium is a lustrous white metal which is malleable and rather harder than lead, being difficult to cut. It retains its lustre in dry air, but in moist air it soon takes up oxygen and becomes coated with a white deposit of quicklime, CaO. When the metal is heated in air the conversion into the oxide is more rapid, and if the heating is sufficiently strong the metal burns with a bright flame.

Calcium decomposes water readily at ordinary temperatures with evolution of hydrogen and formation of calcium hydroxide—

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

When calcium is heated in *nitrogen* to dull redness rapid combination takes place, the metal becoming incandescent. The product is calcium nitride, Ca_3N_2, a dark yellow crystalline substance—

$$3Ca + N_2 = Ca_3N_2.$$

378. **Calcium Oxide and Hydroxide.**—*Calcium monoxide*, CaO, is usually obtained by igniting limestone, mixed with coal, in a kiln. It is termed "quicklime," and when brought into contact with water combination takes place, and a considerable amount of heat is evolved, calcium hydroxide, $Ca(OH)_2$, being formed. The lumps of lime fall to powder when thus treated, "slaked" lime being produced; with sufficient water to bring it to a creamy consistency "milk of lime" is produced.

Lime is manufactured on the large scale by two processes, the continuous and the periodic. In the former limestone and coal are fed in continuously at the top of the kiln, and lime is withdrawn at the bottom—mixed, of course, with some ash. To obtain a lime free from ash, the fuel is sometimes burnt at the side of the kiln, so that only gases pass up through the kiln. In the periodic process large blocks of limestone are built up in an arch above the fire-grate; the kiln is then filled up with limestone in lumps of gradually increasing size. A fire is kept up below the arch for one or two days, and the kiln is then allowed to cool and the lime removed. This process is not so economical as the continuous one, but the kilns are simpler and more easily repaired.

Calcium oxide, or lime, is infusible even in the oxy-hydrogen blowpipe. It dissolves at ordinary temperatures in about 700 parts of water; the limewater so formed has an alkaline reaction, and readily absorbs carbon dioxide, becoming transformed into the carbonate.

Ordinary mortar is made by mixing lime in the moist state with three or four times its weight of sand. The hardening of mortar is due to its gradual transformation into carbonate, and to some extent silicate; and it has been found that the setting of mortar takes place more rapidly when carbonaceous matter, or ammonium carbonate, is brought into intimate admixture with it. Certain siliceous limestones, when burnt, form hydraulic mortar or cement which possesses the property of hardening under water. Portland cement, for instance, contains over 20 per cent. of silica as well as about 10 per cent. of the oxides of alumina and iron.

379. **Calcium Hydride, CaH_2.**—This was the first of the series of metallic hydrides obtained by Moissan. To prepare it crystallised calcium is placed in a nickel boat which is heated to dull redness in an atmosphere of dry hydrogen. The product is a white fused mass with crystalline structure, and consists of an aggregate of slender transparent plates of sp. gr. 1·57. It does not dissociate at 600° C. It is decomposed by water, forming $Ca(OH)_2$ and H_2. The distinctly saline appearance of this substance, like that of the hydrides of the alkali metals already described, argues for the non-metallic character of hydrogen.

380. **Calcium Chloride, $CaCl_2$,** is obtained as a waste product in several important large scale processes, *e.g.* in the production of soda by the ammonia-soda process, and in the manufacture of potassium chlorate. It is prepared on a small scale by acting on lime or calcium carbonate with hydrochloric acid. When exposed to air the anhydrous chloride readily deliquesces, and it is employed in the laboratory for drying gases. It is extremely soluble in water, and boiling saturated solutions deposit crystals of the composition $CaCl_2.6\,H_2O$ on cooling. When the crystals are dissolved in water a large amount of heat is absorbed, while solution of the anhydrous salt in water evolves heat. Like many other chlorides (*e.g.* those of Ag, Hg, Cu) it takes up ammonia in a definite amount, forming $CaCl_2.8\,NH_3$.

381. **Bleaching Powder.**—If chlorine be passed into milk of lime kept cool, calcium hypochlorite, $Ca(OCl)_2$, is formed—

$$2\,Ca(OH)_2 + 2\,Cl_2 = Ca(OCl)_2 + CaCl_2 + 2\,H_2O.$$

If hot milk of lime is used, calcium chlorate, $Ca(ClO_3)_2$, is formed—

$$6\,Ca(OH)_2 + 6\,Cl_2 = 5\,CaCl_2 + Ca(ClO_3)_2 + 6\,H_2O.$$

If, however, *dry* slaked lime be exposed to an atmosphere of chlorine, it takes up about 37 per cent. of its weight of chlorine, and forms "bleaching powder," some of the lime remaining unaltered. Bleaching powder is largely used for bleaching cotton goods and paper pulp, and on the commercial scale is prepared by passing chlorine (usually obtained by the action of manganese dioxide on hydrochloric acid) into large chambers about 6 feet high, on the floor of which the lime is spread to the depth of about 5 or 6 inches.

The constitution of bleaching powder has been the subject of much discussion. Formulae were at first ascribed representing it as containing calcium chloride. It has, however, been found that—

(1) The *whole of the chlorine* may be expelled from it by exposure to moist carbon dioxide at 70° C., whereas calcium chloride is not decomposed by carbon dioxide.

(2) It is not deliquescent ($CaCl_2$ is).

(3) Though calcium chloride is freely soluble in alcohol, an alcoholic extract of bleaching powder is only found to contain traces of chloride.

Odling suggested that bleaching powder consists of calcium chloro-hypochlorite, $Ca(OCl)Cl$, combined with slaked lime, and this formula may be accepted for general purposes though the constitution cannot even now be considered as settled. It is found that the "available" chlorine in bleaching powder, *i.e.* the chlorine which is expelled by the action of dilute acids, amounts to $43\frac{1}{2}$ per cent. and no more in samples which have been most carefully saturated. This is in agreement with the formula $[Ca(OCl)Cl]_2.Ca(OH)_2$.

On treatment with water, bleaching powder is decomposed, forming calcium hypochlorite and chloride—

$$2\,Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2.$$

On treatment with dilute acids it evolves chlorine, hypochlorous acid being formed as an intermediate product. Thus if dilute HCl is used we have—

$$(a)\ 2\ HCl + Ca(OCl)_2 = 2\ HClO + CaCl_2.$$

$$(b)\ 2\ HCl + 2\ HClO = 2\ H_2O + 2\ Cl_2.$$

The reactions with sulphuric acid are—

$$(a)\ CaCl_2 + Ca(OCl)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + 2\,HCl + 2\,HClO.$$

$$(b)\ 2\,HCl + 2\,HClO = 2\,H_2O + 2\,Cl_2.$$

The material to be bleached is first thoroughly cleaned, then soaked in a dilute solution of bleaching powder, and afterwards washed out with dilute acid, when the above reactions take place. Bleaching powder is used for bleaching cotton, linen, and paper, but not for wool, as it destroys the wool fibre.

On distilling a solution of bleaching powder with dilute HNO_3, hypochlorous acid is evolved; it is derived from the hypochlorite formed on dissolving the powder in water.

$$Ca(OCl)_2 + 2\,HNO_3 = Ca(NO_3)_2 + 2\,HClO.$$

Heated with a small quantity of cobalt oxide, Co_2O_3, bleaching powder evolves oxygen, the metallic oxide acting as a catalytic agent. The process is actually carried out by making the bleaching powder into a paste with water, adding a little cobalt nitrate solution and warming. The cobalt nitrate reacts with the bleaching powder, forming the oxide Co_2O_3 (probably). This oxide is unstable and at once loses oxygen—

$$Co_2O_3 = 2\,CoO + O_2.$$

CoO is then converted into Co_2O_3 again by the bleaching powder—

$$Ca(OCl)Cl + 2\,CoO = CaCl_2 + Co_2O_3.$$

This loses oxygen again; forming CoO and so on, the cycle of changes being repeated.

We see then that bleaching powder may, under suitable conditions, be made to yield *chlorine, hypochlorous acid,* and *oxygen.*

Bleaching powder solution acts as a convenient oxidising agent for some purposes, and it is upon this property that the estimation of the "available" chlorine in bleaching powder depends. A standard solution of sodium arsenite is added to one of bleaching powder till the liquid gives no reaction with iodised starch paper. The arsenite is thus oxidised to arsenate.

$$2\,Na_3AsO_3 + Ca(OCl)_2 = 2\,Na_3AsO_4 + CaCl_2.$$

The oxidising action of bleaching powder solution may be employed to prepare lead and manganese peroxides from their salts.

Exp. 204.—Boil a solution of lead acetate with one of bleaching powder for some time. The puce-coloured oxide, PbO_2, will be deposited and should be filtered off, washed repeatedly with hot water and dried.

Repeat with a solution of a manganous salt, and note the formation of the black oxide, MnO_2. If the boiling is long continued and the bleaching powder is in excess, a green solution of manganate may form and ultimately a pink one of permanganate.

382. **Calcium Sulphate, $CaSO_4$.**—This salt occurs as *anhydrite,* $CaSO_4$, and as gypsum, $CaSO_4.2H_2O$. The latter substance is found associated with rock salt, where it occurs as thin bands or seams. *Selenite,* used for optical work, has the same composition as gypsum, but the crystals are usually larger and well formed. Calcium sulphate may be precipitated by the addition of a soluble sulphate to a solution of a calcium salt. It possesses the singular property (slaked lime resembles it in this respect) of being somewhat less soluble in hot water than cold, requiring over 500 parts of water at 100° C., but only 400 parts at 35° C. to dissolve it.

When water containing calcium sulphate is used in boilers, a firm, coherent deposit of the salt gradually forms on the inner surface of the boiler. When gypsum is heated to about 140° C. it loses three-quarters of its water of crystallisation, and is converted into *plaster of Paris,* $2\,CaSO_4.H_2O$; and when this is made into a paste with water it gradually hardens, and hence is used for making casts and for mouldings Calcium sulphate is very much more soluble in hydrochloric acid than in water.

The permanent hardness of water is very frequently caused by the presence in it of dissolved calcium sulphate (see § 114)

383. **Calcium Orthophosphate, $Ca_3(PO_4)_2$.**—This is the most important of the phosphates of calcium; it occurs in bone and in mineral concretions known as "coprolites"; also, associated with chloride and fluoride respectively, as chlorapatite, $3\ Ca_3P_2O_8.CaCl_2$, or fluorapatite, $3\ Ca_3P_2O_8.CaF_2$. The phosphate is only slightly soluble in water, though readily in acids, and is precipitated when a soluble phosphate, such as sodium phosphate, is added to the aqueous solution of a calcium salt in the presence of ammonia. The "superphosphate of lime," used as a manure and for the preparation of phosphorus, is obtained by acting upon calcium phosphate (bone-ash) with sulphuric acid. It is a mixture of the acid calcium phosphate, $CaH_4P_2O_8$, with calcium sulphate.

384. **Calcium Carbonate, $CaCO_3$.**—The mineral forms are known as calcite, crystallising in the rhombohedra, and arragonite, crystallising in rhombic prisms. Soluble calcium salts also yield a precipitate of the carbonate when treated with ammonium carbonate, and it is also obtained synthetically by the action of carbon dioxide on lime, or on lime-water. It is practically insoluble in water, but soluble in an aqueous solution of carbon dioxide with the formation of the bicarbonate $Ca(HCO_3)_2$, and in mineral acids, which latter, however, decompose it. It is found in many natural waters, being held in solution as $Ca(HCO_3)_2$ by the excess of carbon dioxide, and as this escapes it becomes deposited as *tufa* or as *stalactites* and *stalagmites*.

Calcium carbonate, when heated above 550° C., is decomposed into carbon dioxide and calcium oxide, but unless the gaseous product is removed as fast as it is liberated decomposition is never complete. Hence it is futile to attempt to determine the carbon dioxide evolved from a given weight of calcite or chalk by heating in a covered crucible. The heat must be long continued and is better in a current of air such as is always present in a muffle furnace, or in a lime-kiln.

The reason for all this is that at a given temperature the carbon dioxide evolved when the carbonate is heated in a closed space attains a definite pressure (called its *dissociation pressure or tension*—the higher the temperature the greater the dissociation pressure of the carbon dioxide), and when this has been reached no further evolution of gas takes place at that temperature. If, however, some of the CO_2 is removed, the pressure is diminished and a further supply is liberated to restore the equilibrium.

If the lime and carbon dioxide are cooled down again in contact with one another they recombine. The decomposition of calcium carbonate by heat is therefore another example of a reversible action and may be represented—

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

385. **Calcium Carbide, CaC_2,** as ordinarily seen is a greyish black solid, and is prepared on the large scale by heating limestone with coke or coal in the electric furnace.

$$CaCO_3 + 4C = CaC_2 + 3CO.$$

The pure substance has, however, been obtained in the form of colourless or yellow crystals.

The most important property of calcium carbide is the fact that when treated with water it yields acetylene, as we have seen in Exp. 169. This property explains its production on the large scale, the acetylene obtained from it being used for lighting purposes (for motor car and cycle lamps, for enriching coal gas, etc.).

ZINC.

386. **Occurrence.**—The chief ores are the *sulphide*, called zinc blende or familiarly "black-jack," the *silicate*, known as electric calamine, and the *carbonate*, termed calamine. The last is the most abundant ore, though all three are used for the extraction of the metal.

387. **Extraction from the Ore.**—This involves two main processes—

(*a*) Calcination or roasting.

(*b*) Reduction.

Calcination.—Calcination proper is employed in the case of calamine for the purpose of expelling the carbon dioxide and moisture. For zinc blende, the operation of roasting is performed, care being especially necessary to transform the sulphide as completely as possible into oxide and at the same time to avoid its passage into the sulphate, as the latter is reduced to sulphide by carbon, instead of to the metal.

Reduction.—Three processes have been largely used: (1) The English process, now entirely given up; (2) the Belgian process; (3) the Silesian process, mostly employed for poor ores. All these depend on coal or carbonaceous matter as the reducing agent, and they differ chiefly in the form and setting of the retorts used for working the charge and in the method of condensing the zinc.

The Belgian Process.—The retorts are of fireclay, circular or elliptical in section, about 3 feet 6 inches long and 9 inches wide, fitted at the mouth after charging with conical clay condensing tubes terminating in an iron nozzle. Sixty to eighty of these retorts are arranged in a furnace, sloping downwards towards the mouth. The charge, consisting of about two parts of the calcined ore (zinc oxide) to one of coal, both in powder and intimately mixed, is laid about 7 inches deep. A bright red heat is kept up for twenty-four hours and the oxide undergoes reduction, with the formation of carbon monoxide which burns at the mouth of the condenser.

$$ZnO + C = Zn + CO.$$

The temperature used being above the boiling point of zinc, the metal passes off in the form of vapour and condenses for the most part in the clay tubes, whilst zinc oxide collects in the iron nozzles. Zinc ores are always associated with cadmium, and this having a lower boiling-point volatilizes first, producing brown fumes (oxide of cadmium), and the stage at which the zinc begins to distil is known by the flame at the mouth of the condenser changing to a greenish colour, and by the brown fume giving place to a white fume of zinc oxide. At this stage the condenser is changed, and the zinc practically free from cadmium collected. The extraction of zinc is accompanied by a loss of from 12 to 20 per cent. of the zinc.

Silesian Process.—The retorts used are flat at the bottom and D-shaped in section and both longer and deeper than those already described. A curved tube passes from the mouth of the retort into a vertical cast-iron tube which acts as condenser. The condensed zinc falls down on to an iron tray. Thirty or more retorts each having a charge of about 5 cwt. are placed in each furnace and heated by gas.

The **Metal** is of a white colour with a bluish cast, and is brittle at ordinary temperatures, but at about 100° to 150° C. it becomes ductile and may be drawn into wire and rolled into sheet; above 200° C. it loses its cohesion and may readily be powdered. The specific gravity of zinc is 6·9.

Commercial zinc contains traces of iron, cadmium, arsenic, and sulphur; it dissolves freely in dilute mineral acids and in strong solutions of caustic alkalies with evolution of hydrogen—

$$Zn + 2\,HCl = ZnCl_2 + H_2$$
$$Zn + 2\,KOH = K_2ZnO_2 + H_2.$$

Pure zinc is almost insoluble in dilute sulphuric acid, owing to the formation of a thin film of hydrogen which protects the surface of the metal. When the metal is impure, electrolytic actions are set up, by which hydrogen is evolved from the impurities, leaving the zinc surface exposed to the action of the acid.

Water at its boiling point is decomposed by zinc. In the condensation of zinc a portion of the product is obtained in fine powder, known as zinc dust and frequently used as a reducing agent. It contains some zinc oxide, from which it may be freed by treatment with very dilute hydrochloric acid. Zinc is largely used for galvanizing iron plate, which when dipped in the molten metal becomes coated with a thin layer of zinc, and is thereby less liable to corrosion when exposed to the atmosphere. Zinc is also used for desilverizing lead, for electric batteries, and for precipitating gold.

388. **Alloys.**—The alloys which contain zinc are very numerous and find wide application.

The most important of these is brass, consisting of copper and zinc, the colour and other physical properties of which vary according to the proportions of its constituents. If it contains over 50 per cent. of zinc it is white and brittle, if over 80 per cent. of copper it is red or reddish yellow. Certain alloys of copper and zinc are known by special names, such as Muntz metal, pinchbeck, Dutch metal. German silver (and nickel silver) is an alloy of copper, zinc and nickel, and the English bronze coinage consists of 95 per cent. of copper, 4 per cent. of tin and 1 per cent. of zinc.

389. **Zinc Oxide, ZnO,** occurs native as red zinc ore, the colour being due to the presence of iron or manganese oxides. It is formed as a white amorphous powder when zinc burns, which it does if heated somewhat above its melting point in air, and this is the method employed for its manufacture. It is also obtained by strongly heating the carbonate or nitrate. It is used as a pigment under the name zinc white, the value of which consists in the fact that it preserves its whiteness in presence of sulphuretted hydrogen (the sulphide being white) or other impurities in air.

The *hydroxide*, $Zn(OH)_2$, is obtained by adding caustic alkalies to zinc salts; excess of the alkali re-dissolves the precipitate with formation of potassium zincate, K_2ZnO_2. In presence of caustic alkalies, therefore, zinc oxide may be regarded as playing the part of an acid-forming oxide. Potassium zincate is also formed when zinc (especially in presence of iron) is heated with a strong solution of caustic potash—

$$Zn + 2\,KOH = K_2ZnO_2 + H_2.$$

390. **Zinc Sulphide, ZnS,** is a white powder, the dark colour of the mineral, blende, being due to the presence of iron; in the hydrated form, it is obtained by the action of sulphuretted hydrogen or ammonium hydrosulphide on the

neutral solution of a zinc salt. It is insoluble in acetic acid, but soluble in mineral acids.

391. **Zinc Chloride, $ZnCl_2$.**—This, as well as the bromide and iodide, may be prepared by the interaction of zinc with the halogen element, or by the action of the halogen acid on the metal, oxide or carbonate. It is extremely soluble in water, even one-third of its weight of water sufficing to produce a thick oily liquid, from which on evaporation the anhydrous substance is obtained as a white solid. It is very deliquescent, and hence a powerful dehydrating agent, attacking many organic substances with the abstraction of water. Zinc chloride has been volatilised, and is found to have a vapour density corresponding to the formula $ZnCl_2$. By boiling its solution with zinc oxide, oxychloride of zinc is formed.

392. **Zinc Sulphate, $ZnSO_4$,** known also as white vitriol, is formed by the action of sulphuric acid on zinc or its oxide or carbonate; also by roasting zinc blende. Three parts of water dissolve four parts of the salt at ordinary temperatures, and on concentration of the solution it separates out in crystals, having the composition $ZnSO_4.7H_2O$.

Exp. 205.—Prepare zinc sulphate from zinc blende by heating the blende in a hard glass tube in a current of air, extracting the product with water, filtering and crystallising out the salt from the filtrate.

393. **Zinc Carbonate, $ZnCO_3$,** occurs, as already stated, in the form of calamine. On the addition of $KHCO_3$ to a zinc salt this (the normal) carbonate is precipitated, but if K_2CO_3 be used, basic carbonates of variable composition are obtained according to the temperature at which the experiment is carried out and the amount of water present.

The soluble normal salts of zinc have an acid reaction to litmus; they are poisonous.

394. **Comparison of Calcium and Zinc.**—The metals calcium and zinc resemble each other in certain important respects: *e.g.* both metals are divalent and form an oxide RO, and salts of the types RCl_2, $R(NO_3)_2$, R_2SO_4,

$R_3(PO_4)_2$. (R = Ca or Zn.) The chlorides and nitrates of both metals are readily soluble in water, whilst the phosphates are insoluble. Zinc sulphate, however, is readily soluble in water, whereas calcium sulphate is only slightly soluble.

On the other hand, the metals differ in many important particulars. For example:

(1) Calcium readily decomposes cold water; zinc does not.

(2) Zinc oxide is easily reduced to the metal by heating with carbon; calcium oxide cannot be so reduced.

(3) Calcium hydroxide is soluble in water, forming an alkaline solution; zinc hydroxide is insoluble.

(4) Zinc exhibits a tendency to form basic salts, especially with weak acids (cp. § 393), which is not shown by calcium.

(3) and (4) illustrate the more strongly basic nature of calcium hydroxide as compared with zinc hydroxide.

The above comparison of calcium and zinc is not intended to be by any means exhaustive, and it will form a useful exercise for the student to complete it on the lines indicated.

QUESTIONS.—CHAPTER XXVIII.

1. Give the names and formulae of the more commonly occurring compounds of calcium found in nature, and state the purposes, if any, for which they have been employed in the arts or manufactures.
2. Compare and contrast the properties of quicklime, slaked lime, and calcium carbonate. How may any one of these substances be converted into the others?
3. What is the chemical nature of ordinary mortar? To what is the hardening of mortar due? How do you account for the difference between "ordinary" and "hydraulic" mortars?

4. What happens when chlorine is passed (*a*) into milk of lime kept cool, (*b*) in excess into the same substance at a high temperature, (*c*) into a vessel containing dry slaked lime?

   Give equations for the reactions in each case and a brief description of the physical and chemical properties of the substances formed.

5. What do you consider to be the formula for bleaching powder? Give reasons for your answer.

6. What is the effect of adding bleaching powder to (*a*) water, (*b*) dilute HCl, (*c*) dilute H_2SO_4? Give equations to express the chemical changes in each case. How would you proceed to bleach a piece of coloured cloth by means of bleaching powder?

7. How could you obtain from bleaching powder (*a*) chlorine, (*b*) hypochlorous acid, (*c*) oxygen, (*d*) calcium chlorate, (*e*) calcium chloride?

8. Bleaching powder is often mentioned as an oxidising agent. Give instances of its use in this capacity.

9. How would you prepare a sample of pure calcium sulphate? In what forms does this substance occur in nature? How does plaster of Paris differ from chemically precipitated calcium sulphate, and on what property does its use as a cement, and for making casts, depend?

10. Give some account of the forms in which calcium carbonate is found in nature. Describe the effect of (*a*) adding dilute hydrochloric acid to the substance, (*b*) shaking the powdered substance with a solution of carbon dioxide, (*c*) strongly heating it.

11. How do you account for the fact that powdered calcite cannot be completely decomposed into carbon dioxide and calcium oxide, when heated in a closed vessel? Describe exactly how you would proceed to determine the weight of CO_2 that could be expelled from calcite by the application of heat.

12. Describe how you would prepare from bones a sample of calcium phosphate, and one of "superphosphate of lime." How do these two substances differ as

regards (*a*) composition, (*b*) their behaviour towards water, (*c*) their behaviour on heating?

13. What is zinc blende? How is metallic zinc obtained from it on the large scale?

14. Give some account of the chief chemical and physical properties of *zinc*.

    Give reasons for and against classifying zinc with calcium.

15. How would you obtain from calamine the chloride, sulphate, and oxide of zinc respectively, and by what means could you reconvert these substances into the substance of which calamine is a more or less impure form?

CHAPTER XXIX.

SILVER AND MERCURY.

SILVER.

395. **Occurrence.**—The chief natural forms are metallic silver, silver glance, Ag_2S, stephanite, $5Ag_2S.Sb_2S_3$, ruby silver ore consisting of sulphides of silver and antimony or silver and arsenic, horn silver, AgCl. Much silver is also extracted from galena. (See § 417.)

396. **Extraction of Silver.**—(1) *By amalgamation.*—Several methods have been described depending on the action of mercury on silver compounds, whereby the silver is dissolved in the mercury, the mercury being separated ultimately from it by distillation. The method now mostly employed is as follows. The ore is finely powdered and mixed into a slime with water; it is then brought into intimate contact with about $\frac{1}{10}$ its weight of mercury for two or three hours and the amalgam separated as completely as possible from the mud in settlers. This amalgam consists of (*a*) solid amalgam containing much silver and (*b*) liquid amalgam which is the excess of mercury containing small quantities of silver. The solid amalgam is submitted at once to distillation, whilst the liquid is used again in the amalgamation process.

In most ores a previous roasting with common salt is desirable in order to convert the silver into a form (AgCl) in which it is readily acted upon by mercury. A great improvement is effected by adding to the mercury about one per cent. of sodium.

(2) *By wet processes.*—(*a*) *Percy-Patera process.*—The ore is transformed first into the chloride by roasting it with common salt, and this chloride is then dissolved out with sodium thiosulphate and the silver finally precipitated as sulphide by the addition of sodium sulphide. The silver

sulphide is then roasted in a reverberatory furnace; the sulphur is removed and metallic silver remains.

(*b*) *Augustin process.*—The ore is roasted with common salt, and the silver chloride produced is dissolved out with strong brine. Silver is precipitated from the solution by means of scrap copper.

(*c*) *Ziervogel process.*—The ore used in this process consists of argentiferous copper pyrites. It is roasted, whereby all the sulphides present, namely, those of silver, copper, iron, and lead are converted into sulphates. If the mixed sulphates be then exposed on the bed of the furnace to a higher temperature, the sulphates of iron and copper are decomposed before the silver sulphate. This latter is then extracted by water and metallic silver precipitated from the solution by means of scrap copper.

(3) *The desilverising of lead.*—About one-third of the silver produced is extracted from lead; the process will be described under that metal. (See § 417.)

397. **Properties of Silver.**—Pure silver is a white metal, lustrous, and capable of taking a high polish and of being hammered or rolled into plate and drawn into wire. These properties of malleability and ductility it possesses in almost as high a degree as gold, so that silver sheet $\frac{1}{10000}$ of an inch thick and wire $\frac{1}{3000}$ of an inch thick may be obtained; its tensile strength is over 17 tons to the square inch of section. Its specific gravity, like that of other metals, varies somewhat according to the treatment to which it is subjected, being about 10·3 to 10·6 in the solid condition and 9·46 in the molten state.

Silver melts at 960° C. and may be distilled at the highest temperature of the oxyhydrogen blow-pipe. The molten metal absorbs about 22 times its volume of oxygen, which it gives up on solidification, giving rise to the phenomenon of "spitting." Spitting is prevented by a layer of charcoal over the silver. Silver is a better conductor of heat and electricity than even copper. By the action of certain reducing agents on silver salts the metal is obtained in a finely divided condition, in which form it shows brilliant golden, ruby, blue, and other tints.

398. **The Oxides and Hydroxides.**—The hydroxide is obtained as a brown powder by adding caustic potash to solutions of silver salts. It is an unstable body and above 100° C. it gradually loses water and passes into the *oxide* Ag_2O, which again decomposes into metallic silver and oxygen at about 300° C. It dissolves in ammonia, and on exposure of the solution to air *fulminating silver* separates out. This body detonates on the slightest friction when it is dry and sometimes even in the moist state. It seems to have the composition Ag_3N. When a solution of silver nitrate is electrolysed, black needles form on the kathode; these vary in composition according to the circumstances under which they are obtained, but give evidence of containing an unstable *peroxide* of silver, Ag_2O_2.

399. **Silver Sulphide, Ag_2S,** is obtained either by heating together silver and sulphur or by precipitating silver salts with sulphuretted hydrogen. It is found in nature as the mineral *silver glance.*

400. **Silver Chloride, AgCl.**—This salt, which occurs native as *horn silver,* is obtained as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to silver salts. Like the bromide of silver it is affected by exposure to sunlight or other chemically active rays; it assumes at first a violet tinge, ultimately dark brown, and undergoes loss of chlorine. Though insoluble in water,* and practically so in mineral acids, silver chloride dissolves readily in ammonia, in solutions of sodium sulphite or thiosulphate, and in potassium cyanide. It dissolves also somewhat easily in alkaline chlorides, and salt brine is often used for the extraction of silver.

The precipitated chloride absorbs ammonia and forms $2AgCl.3NH_3$, and a similar body separates in octahedral crystals out of a saturated solution of silver chloride in ammonia. The chloride is reduced to metallic silver by the action of zinc in presence of dilute sulphuric acid, by heating it in a current of hydrogen or by fusion with alkaline carbonates or in presence of organic substances.

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* It appears that the curdy form of AgCl is soluble to a very slight extent in cold water, and appreciably so in hot. The fused substance only appears to be practically insoluble.

At a temperature of about 1700° C. silver chloride can be volatilised, and its vapour density corresponds to the formula $AgCl$. According to Ramsay the molecule of silver is monatomic.

The *bromide*, $AgBr$, and *iodide*, AgI, are both found native in Mexico and Chili. The bromide dissolves in ammonia, though less freely than the chloride, and the iodide is almost insoluble in ammonia. The iodide is nearly insoluble in alkaline chlorides, and hence, when salt brine is used for the extraction of silver, the silver iodide may be thrown down by the addition of a soluble iodide. Though insoluble in a solution of ammonia, the dry iodide takes up large quantities of gaseous ammonia, forming $2AgI.NH_3$.

Exp. 206.—To a solution of silver nitrate add HCl. Show the solubility of the precipitated $AgCl$ in ammonia, and its reprecipitation with nitric acid. Also show its solubility in a strong solution of common salt and the precipitation of silver iodide from this solution by the addition of potassium iodide.

401. **Silver Sulphate, Ag_2SO_4,** is formed by dissolving the oxide or carbonate in sulphuric acid. It dissolves in about 200 times its weight of cold water, but is much more soluble in hot. It crystallises in prisms similar in form to those of anhydrous sodium sulphate. The existence of a silver hydrogen sulphate, $AgHSO_4$, and a silver alum, $Ag_2SO_4.Al_2(SO_4)_3.24\,H_2O$, corresponding to ordinary alum, $K_2SO_4.Al_2(SO_4)_3.\,24\,H_2O$, further exhibits the relationship of silver with the alkali metals. Silver sulphate forms a compound with ammonia, of the composition $Ag_2(NH_3)SO_4$.

402. **Silver Nitrate, $AgNO_3$,** is obtained by dissolving the metal in nitric acid. It readily dissolves in water, and is the form in which silver is most frequently employed as a reagent. It possesses a powerful corrosive action on organic tissues, which are stained black by it; it acts also similarly on vegetable fibre, and is used as the basis of many preparations of "marking ink." Dry silver nitrate absorbs

ammonia, forming $AgNO_3.2NH_3$; it also forms double salts with nitrates of the alkalies, *e.g.* $KNO_3.AgNO_3$, $NH_4NO_3.AgNO_3$, these being formed as crystals by bringing together solutions of the respective nitrates, and allowing them to evaporate slowly.

Exp. 207.—Dissolve a silver coin in nitric acid, dilute with water, and precipitate silver chloride with HCl. Wash the precipitate repeatedly by decantation till it is free from copper and HCl. Reduce the precipitate to metallic silver by warming either with caustic potash and grape sugar, or with zinc and dilute sulphuric acid. Wash the precipitated silver, dissolve in pure nitric acid, evaporate to dryness, then add water and obtain crystals of silver nitrate.

403. **Silver Carbonate, Ag_2CO_3,** is an unstable white powder, obtained by precipitating silver nitrate with an alkaline carbonate. If silver nitrate be treated with potassium carbonate in presence of carbon dioxide, $AgKCO_3$ is obtained.

MERCURY.

404. **Occurrence.**—Although occasionally found in small quantity in the free state, the sulphide HgS, cinnabar, is by far the most important source of mercury. The chief localities where the extraction is carried on are Idria in Austria, Almaden in Spain, and in the neighbourhood of San Francisco, California.

405. **Extraction from the Ore.**—The process of extraction is an extremely simple one, and consists usually in roasting the ore in a reverberatory furnace, or even a small blast furnace, with access of air by which the sulphur is oxidised to sulphur dioxide, and the mercury set free and volatilised.

$$HgS + O_2 = Hg + SO_2.$$

Sometimes lime or oxide of iron ("smithy scales") is mixed with the ore, and the sulphur retained in this way as sulphide of lime or iron respectively. The condensation of the vapours of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in the different localities.

At Idria, the vapours are passed through a series of chambers in which the metal condenses and from which it flows away into suitable receptacles. In Almaden twelve parallel series of conical clay receivers called "aludels," luted together, are interposed between the furnace and the flue; each of these is about twenty inches long, and a series extends about twenty yards. The lines of aludels are of sufficient length to allow the vapours and gases to cool down nearly to the temperature of the air, and so arranged as to allow the condensed mercury to gravitate towards a common channel, where it collects.

406. The **metal** thus obtained contains small quantities of lead, bismuth, zinc, etc.; it may be purified by distillation in vacuo, or by treatment with dilute nitric acid, which dissolves out the impurities. It has a specific gravity of 13·6, and is the only metal that is liquid at the ordinary temperatures; it possesses a silvery lustre; at − 39° C. it becomes solid, and in this form it is malleable. Even at ordinary temperatures it has a small vapour tension, and gives off minute quantities of its vapour into the atmosphere in contact with it; it boils at about 360° C. When heated almost to its boiling point in air it becomes coated with the red oxide, HgO; ozone oxidises it superficially at ordinary temperatures.

Mercury is largely used in the extraction of silver and gold, in making barometers, thermometers, and other scientific apparatus, and for preparing compounds of mercury, which are important in medicine.

Amalgams.—With most of the metals mercury forms alloys (amalgams), and in some cases these amalgams possess a definite composition, and crystalline form, *e.g.* Hg_5Na is brittle, and crystallises in the regular system. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water hydrogen is evolved.

Exp. 208.—Make some sodium amalgam by dissolving sodium in mercury, and examine its action on water.

Tin amalgam is used for producing the silvery coating on glass for mirrors.

Mercury forms two series of compounds, the *mercurous* and the *mercuric*; apparently the metal is *divalent* in both groups, the mercurous compounds containing two atoms of mercury in the molecule, each of which saturates one valency equivalent of the other. It will be seen that the two series differ very considerably in properties.

407. **Mercurous Oxide, Hg_2O,** is a dark brown powder obtained by digesting calomel (Hg_2Cl_2) with caustic potash; it is unstable, and is even decomposed by the action of light with the production of mercuric oxide and mercury.

Mercuric Oxide, HgO, exists as a crystalline red powder obtained by heating the metal in air, or by calcining the nitrate. It is also obtained as a yellow powder by the addition of caustic alkalies to mercury salts, and in this form, by reason of its finely divided state and the readiness with which it parts with oxygen, the oxide is an active oxidising agent. The yellow oxide is changed into the red by heating to about 400° C. The red oxide when heated turns black, and at a higher temperature decomposes into the metal and oxygen; it is slightly soluble in water, and has an alkaline reaction.

408. **Mercuric Sulphide, HgS,** is formed as a black amorphous powder by triturating mercury and sulphur together, or by precipitating solutions of mercuric salts with sulphuretted hydrogen. It occurs native in dark red crystals, and in this form is called cinnabar. It is also prepared artificially as a bright red crystalline powder, the pigment vermilion. This is prepared either by the *dry process*, in which a mixture of mercury and sulphur is heated, or by the *wet process*, in which amorphous sulphide of mercury is exposed to the action of alkaline sulphides. Exceptional brightness of tint and degree of fineness are attained only by attention to technical detail in the preparation.

409. **Mercurous Chloride or Calomel, Hg_2Cl_2,** is found as the mineral horn-quicksilver and is produced artificially—

(1) By the direct union of mercury with chlorine.

(2) By the addition of hydrochloric acid or a soluble chloride to a solution of a mercurous salt.

(3) By the action of certain reducing agents such as phosphorous acid or stannous chloride on mercuric chloride.

(4) By triturating or heating mercuric chloride with metallic mercury.* The latter is the manufacturing method.

Calomel is an amorphous white powder insoluble in water and acids; it can be brought into solution (as *mercuric* chloride) by the action of strong nitric acid or aqua regia or by prolonged digestion with dilute nitric acid. If heated alone it sublimes, but in contact with carbon it undergoes reduction to metallic mercury.

The vapour obtained by heating calomel under ordinary conditions is a mixture of mercury and mercuric chloride, but Baker, using the apparatus already described under ammonium chloride (§ 373), has shown quite recently that if the mercurous chloride is thoroughly dried before being vaporised and the pure substance employed there is very little dissociation. He experimented with some pure mercurous chloride which he dried with P_4O_{10} for three weeks. The mean of five experiments gave 217 as the vapour density. The formula Hg_2Cl_2 requires 235.

When ammonia is added to mercurous chloride a black substance is formed. This has been shown to consist of a mixture of dimercurammonium chloride, NHg_2Cl, with finely divided mercury which gives it the black colour, the chloride being yellow.

410. Mercuric Chloride, Corrosive Sublimate, $HgCl_2$.— Corrosive sublimate is made on the large scale by heating 5 parts of mercuric sulphate with 2 parts of common salt—

$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4$$

and finally separating the mercury salt by sublimation.

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* It may in general be taken that in the preparation of salts of mercury, if the metal be kept in excess the *mercurous* salt is obtained, whilst if the acid be concentrated and in excess the *mercuric* salt will be obtained, and that the latter will be converted into the former by trituration with excess of the metal.

It is readily soluble in water, alcohol or ether, and in presence of hydrochloric acid or alkaline chlorides it forms double salts such as $HgCl_2.3HCl$ and $HgCl_2.2NH_4Cl.H_2O$. It also shows a tendency to form oxychlorides, which are obtained by digesting the solution with mercuric oxide.

It crystallises from a hot solution in needles which melt at 288° C. and at about 300° C. become transformed into vapour. The compound is extremely poisonous, but in small doses it is a valuable medicine; its solution possesses also powerful antiseptic properties.

When ammonia is added to a solution of mercuric chloride a white precipitate is formed having the composition represented by the formula, NH_2HgCl; it is called *infusible white precipitate.* When this compound is boiled with ammonium chloride it dissolves and the solution on cooling deposits crystals of *fusible white precipitate*; this may be regarded as a compound of mercuric chloride and ammonia, $HgCl_2.NH_3$.

411. **Mercurous Iodide, Hg_2I_2, and Mercuric Iodide, HgI_2,** are obtained by triturating mercury and iodine together, the former resulting when excess of mercury is used, and the latter if the iodine is in excess. Mercuric iodide is also obtained as a brilliant red precipitate, by mixing solutions of potassium iodide and mercuric chloride, the precipitate being soluble in excess of either reagent. If the potassium iodide be added until the red precipitate is just redissolved (with formation of K_2HgI_4), and if this be followed with caustic soda, *Nessler's solution* is obtained, and this is an extremely sensitive reagent for detecting the presence of ammonia. Minute traces of ammonia give a yellowish-brown coloration and greater quantities yield a brown precipitate—

$$2\,K_2HgI_4 + 3\,NaOH + NH_3 = NHg_2I.H_2O + 4\,KI + 3\,NaI + 2\,H_2O.$$

Exp. 209.—Prepare Nessler's solution and examine its action on water containing very small quantities of ammonia.

The scarlet iodide of mercury when heated passes into a bright yellow form, which is, however, unstable and returns to the red form again, slowly on standing, or immediately by rubbing it.

412. **Mercurous Sulphate, Hg_2SO_4, and Mercuric Sulphate, $HgSO_4$**, are obtained by heating together mercury and sulphuric acid, the mercurous or mercuric compound being produced according as excess of mercury or sulphuric acid respectively is used. The mercuric sulphate is the more important salt; it consists of white crystals which on heating undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is very liable to become basic; *turpeth mineral* is a yellow basic sulphate, $2\,HgO.HgSO_4$, obtained by digesting mercuric sulphate with boiling water.

413. **Mercurous Nitrate, $Hg_2(NO_3)_2$, and Mercuric Nitrate, $Hg(NO_3)_2$**, are formed from mercury and nitric acid under similar conditions to the sulphates, and like them form basic salts in presence of water.

For the weaker acids the affinity of Hg is too small to allow the formation of stable salts; the phosphates, carbonates, borates, and silicates have been either not prepared at all, or obtained as basic compounds of variable composition.

414. **Comparison of Silver and Mercury.**—These two metals resemble each other in a number of points, *e.g.*—

(1) Their compounds are very easily reduced to the metallic state.

(2) They form compounds of similar composition, *e.g.* Ag_2O, Hg_2O; Ag_2SO_4, Hg_2SO_4.

(3) Both metals are unacted upon by water, by the halogen acids, or by dilute sulphuric acid, but are converted into salts by nitric acid and by hot concentrated sulphuric acid.

(4) AgCl and Hg_2Cl_2 are both insoluble in water, and both of them absorb ammonia gas.

On the other hand, these metals differ in many respects, *e.g.*—

(1) Silver only forms one series of salts, mercury forms two.

(2) Mercury exhibits a strong tendency to form basic salts; silver forms very few basic salts.

(3) Mercury takes up oxygen when heated in air at a suitable temperature; silver will not unite directly with oxygen.

The student should complete the comparison of the two metals on the lines indicated above.

QUESTIONS.—CHAPTER XXIX.

1. What are the chief naturally occurring compounds of silver? Give some account of the methods in use at present for the extraction of the metal from its ores.
2. Describe and explain what occurs when (*a*) ammonia, (*b*) potash is carefully added to a solution of a silver salt.
3. Give as full an account as you can of the physical and chemical properties of silver chloride. How could you prepare metallic silver from it? Describe and explain the action upon silver chloride of ammonia, water, sodium thiosulphate, potassium chloride respectively.
4. Starting with metallic silver, how would you prepare (*a*) silver nitrate, (*b*) silver chloride, (*c*) silver oxide, (*d*) silver hydroxide?
5. How would you prepare pure silver sulphate from a silver coin?
6. In what forms is mercury found in nature? How is it usually extracted? Describe its chief physical and chemical characteristics. What do you understand by the term "amalgam"?
7. Describe methods of preparing the oxides of mercury (*a*) from the metal, (*b*) from its compounds.

8. How are the two chlorides of mercury prepared? Compare their behaviour towards water and acids; also compare the action of heat on them. What is the evidence for the formula Hg_2Cl_2 for the lower chloride?
9. What happens when potassium iodide solution is added drop by drop to excess of mercuric chloride, and when the latter substance is added similarly to potassium iodide solution? What is *Nessler's solution,* how is it prepared, and for what purpose is it used?
10. Discuss the action of (*a*) sulphuric acid, (*b*) nitric acid on mercury.
11. Give reasons for and against classifying silver and mercury together.

CHAPTER XXX.

LEAD.

415. **Occurrence.**—The chief ore from which lead is extracted is galena, PbS. It is very widely distributed and is worked in various parts of the United Kingdom, especially in the northern and south-western counties of England, in Flintshire, and in the Leadhills, Scotland. On the Continent, lead is extracted in the Harz, in Carinthia, Spain, Belguim, and other localities; in parts of America, Australia, and Africa there are also considerable deposits of lead ores. The less common ores are cerussite, $PbCO_3$, pyromorphite, $3Pb_3(PO_4)_2.PbCl_2$, and anglesite, $PbSO_4$.

416. **Metal.**—In treating of the metallurgy of lead we shall deal with the methods employed in its extraction from galena as the chief source of the metal. The first part of the process is carried on in a reverberatory furnace at a moderate temperature whereby *part* of the galena is converted into oxide and sulphate—

$$(1) \quad 2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2;$$

$$(2) \quad PbS + 2\,O_2 = PbSO_4.$$

The temperature is then raised and the remaining sulphide reacts by double decomposition with the oxide and sulphate formed in the first stage—

$$(3) \quad PbS + 2\,PbO = 3\,Pb + SO_2;$$

$$(4) \quad PbS + PbSO_4 = 2\,Pb + 2\,SO_2.$$

With the exception of about 10 per cent. which remains in the "slags," the lead is thus obtained in the metallic condition. After running off the lead the residue in the slags is extracted by adding lime and a little coal and submitting the mixture to further heating.

The essential elements in the construction of the furnace (Fig. 91) are:—

(A) The hopper at which the charge is introduced.

(B) The fire-place at one end and separated from the hearth by a rather high fire-bridge.

(C) The hearth formed by moulding slag into the form shown, the depression serving for the collection of the molten lead, and the slopes of the hearth for spreading the charge so as to expose it to the action of the fire gases and for working the slags.

(D) The doors for regulating the supply of air and working the charge.

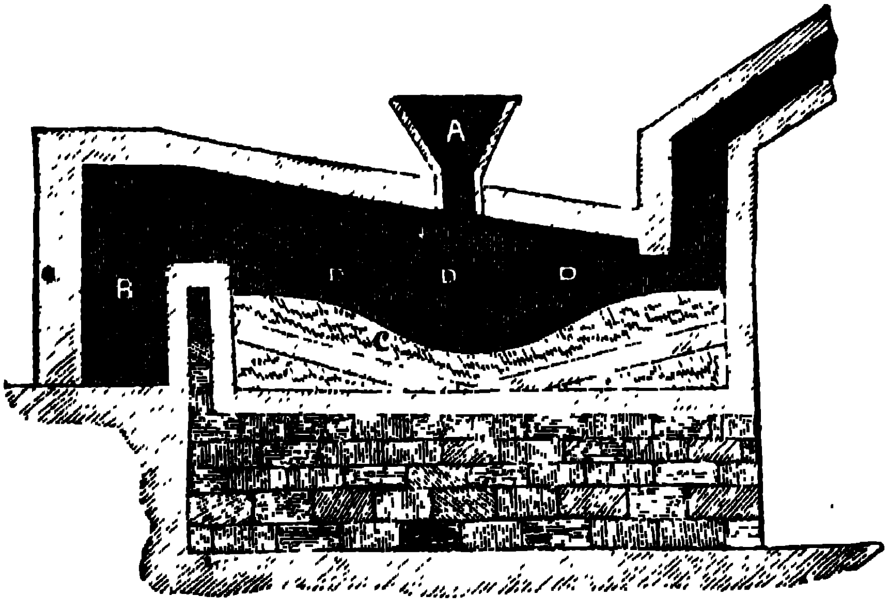

FIG. 91.

The first part of the process is carried out at dull red heat, and is essentially one of calcination and oxidation, during which reactions (1) and (2) take place. The doors are then closed and the temperature raised to a full red heat, when reactions (3) and (4) are effected.

The lead obtained frequently contains sufficient antimony (as well as tin, copper, iron, silver, etc.) to render it hard, and it is in this case submitted to a process of *softening*. The metal is heated on the bed of a reverberatory furnace until the antimony (copper, etc.) becomes oxidised and forms a scum on the surface. This is skimmed off along with litharge which collects with it, and the process continued until the lead shows the proper degree of softness.

417. **Desilverising Lead.**—Lead frequently contains silver in sufficient quantity to make it worth recovering.

One process by which this is carried out is known as the *Pattinson process* which depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. By melting the lead and then by sprinkling water upon it to bring down its temperature just to the solidifying point, the purer lead crystallises out first, and if this be removed by a perforated ladle, the liquid remaining is richer in silver. By repeating the treatment the silver accumulates, until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by *cupellation.*

This consists in heating the metal in an oxidising atmosphere on a *cupel, i.e.* in a special furnace, the bed of which is made of bone-ash impregnated with pearl-ash. The lead is oxidised to litharge, which collects at the surface of the charge and is partly blown off, partly absorbed by the bed of the furnace, carrying with it the impurities and leaving molten silver.

418. **Properties of the Metal.**—Lead is a soft bluish-grey metal with a bright lustre at a freshly-cut surface. Such a surface, however, soon tarnishes in air. It is very malleable but possesses very little tenacity. The specific gravity of lead varies from 11·25 to 11·39 according to the treatment to which it has been subjected. Its melting point is 326° C.

The metal dissolves readily in nitric acid, forming lead nitrate; it is only acted on slowly by hydrochloric acid even in presence of air; sulphuric acid only acts on lead when hot and concentrated.

Action of Water upon Lead.—If a sheet of lead having a bright surface be placed in ordinary distilled water and left for a time, the surface layer becomes oxidized, through the combined action of the water and dissolved air, to lead hydroxide $Pb(OH)_2$, which dissolves in the water. This process will be repeated, and under favourable circumstances a considerable quantity of lead hydroxide will form. This usually becomes converted by CO_2 derived from the atmosphere into basic lead carbonate which appears as a precipitate. Excess of carbon dioxide would cause some of this substance to pass into solution owing to the formation of a soluble bicarbonate. We see then that it is possible for even distilled water to dissolve lead. This action is aided by the presence of bicarbonates, nitrates and ammonium salts in the water, since these tend to the formation of soluble lead compounds.

If on the other hand a sulphate is present in the water, a film of insoluble lead sulphate is formed on the surface of the metal, which protects it from the further solvent action of the water. Hence waters containing sulphates are safe from lead poisoning. Distilled water from which all dissolved gases have been expelled exerts no solvent action upon lead.

Exp. 210.—Investigate the action of (*a*) recently-boiled distilled water, (*b*) ordinary distilled water, (*c*) solutions of various salts, on lead by placing the liquids in test-tubes in contact with pieces of lead, corking up the tubes, and leaving them for a week. Then test the liquids for lead by means of H_2S. and compare the depth of coloration or the amount of precipitate produced under the different conditions. N.B. The tube containing distilled water should be *quite full* of liquid, as air must be excluded.

Alloys.—Lead is an essential constituent of several common alloys. *Solder* is an alloy of lead and tin, the proportions of the metals used varying between the limits 2 parts of tin to 1 part of lead and 2 parts of lead to 1 of tin; *pewter* is an alloy of 1 part of lead to 4 of tin; *type metal* is composed of 4 parts of lead to 1 of antimony; and an alloy of these metals with the antimony predominating is used in the construction of appliances where resistance to the action of strong acids is called for.

419. Oxides and Hydroxides.—**Lead monoxide, PbO,** called also massicot and litharge, is obtained when metallic lead is oxidised at high temperatures, the massicot being a dull yellow powder and the litharge (obtained in the cupellation process) a flaky mass, varying in colour from pale yellow to reddish. When a solution of lead oxide in caustic potash is allowed to cool slowly, a yellow oxide crystallises out, whilst if the cooling be still more gradual, reddish crystals of a different form are obtained. The oxide is used in the production of flint glass and of glaze for pottery.

When ammonia is added to solutions of the salts of lead, the *hydroxide*, $Pb(OH)_2$, is precipitated. This hydroxide is somewhat soluble in water with an alkaline reaction, and, like the caustic alkalies, it absorbs carbon dioxide.

420. **Red Lead** or **Minium, Pb_3O_4,** is prepared by the oxidation of massicot, a moderate temperature and free contact with air being essential to its production. When red lead is strongly heated, it becomes darker in colour, and ultimately gives up a part of its oxygen, forming the monoxide. When treated with dilute nitric acid, a brown powder, *lead dioxide*, PbO_2, is left as a residue. This has led to the view that red lead should be regarded as a compound of the monoxide and the dioxide $(PbO)_2.PbO_2$. The action of nitric acid is then—

$$(PbO)_2.PbO_2 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O.$$

Similarly the *sesquioxide*, Pb_2O_3, may be regarded as $PbO.PbO_2$, and this likewise yields the dioxide on treatment with dilute nitric acid.

421. **Lead Dioxide** or **Peroxide, PbO_2,** is a brown powder obtained, as already described, by adding dilute HNO_3 to red lead; also by the action of chlorine on the monoxide suspended in caustic soda or potash, or on a solution of a lead salt (such as lead acetate) in presence of free alkali. In each of these cases the alkali and chlorine may be supposed to form a hypochlorite, which then oxidises the lead compound

$$PbO + NaOCl = NaCl + PbO_2.$$

$$\underset{\text{Lead acetate}}{2\ Pb\ (C_2H_3O_2)_2} + 2\ KOCl + 2H_2O$$

$$= 2\ PbO_2 + 2\ KCl + \underset{\text{Acetic acid}}{4\ H.C_2H_3O_2}.$$

When strongly heated lead dioxide gives off oxygen, and passes ultimately into the monoxide. It combines directly with sulphur dioxide, forming lead sulphate with such energy that the product becomes red hot. If lead dioxide be fused with caustic potash, direct combination takes place with the formation of potassium plumbate, K_2PbO_3. The formation of this compound shows that lead may act as an acid-forming element towards strong bases. With hydrochloric acid lead dioxide behaves like manganese dioxide, evolving chlorine—

$$PbO_2 + 4\,HCl = PbCl_2 + Cl_2 + 2\,H_2O,$$

and with sulphuric acid it evolves oxygen—

$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O + O_2.$$

Lead dioxide is used in the manufacture of matches, and also as an oxidising agent in the production of aniline dyes.

422. **Lead Sulphide, PbS,** is obtained by direct union of the elements, or by the action of sulphuretted hydrogen on solutions of lead salts. By the action of nitric acid, or even by exposure of the moist sulphide to air at the ordinary temperature, it becomes oxidised to *lead sulphate*, $PbSO_4$. Hydrogen peroxide also brings about the same change as we saw in § 122.

423. **Lead Chloride, $PbCl_2$,** is the white precipitate formed when hydrochloric acid or a soluble chloride is added to a solution of a salt of lead. It is slightly soluble in cold water, but much more freely in hot water, from which on cooling the chloride separates in glittering plates. Several basic chlorides are formed either by the addition of ammonia or lime water to solutions of lead chloride, or by fusing oxide of lead with the chloride. One of these, Pb(OH)Cl, known as Pattinson's white, is used as a pigment, and is obtained by boiling milk of lime with chloride of lead.

A hot solution of lead chloride containing excess of hydrochloric acid gives with sulphuretted hydrogen a reddish precipitate which is a double compound of lead chloride and lead sulphide, probably having the composition $PbS.PbCl_2$. It often appears in the ordinary process of qualitative analysis, and is due as stated above to the presence of $PbCl_2$ and excess of HCl. Excess of sulphuretted hydrogen converts it into the black sulphide.

Lead chloride is volatile at high temperatures, and at about 900° C. its vapour density corresponds to the formula $PbCl_2$.

The **Tetrachloride, $PbCl_4$**, is a very unstable body obtained by the action of chlorine on the dichloride suspended in hydrochloric acid. With ammonium chloride it forms a double salt of the composition $2(NH_4)Cl.PbCl_4$, or $(NH_4)_2PbCl_6$ (*cf.* $(NH_4)_2PtCl_6$), and this on addition of cold concentrated sulphuric acid yields the tetrachloride again. This affords a means of obtaining the substance in a fairly pure condition.

The **Bromide, $PbBr_2$**, and **Iodide, PbI_2**, are, like the chloride, obtained by acting on the salts of lead with the respective acids or their soluble salts. They also resemble the chloride in being much more soluble in hot water than cold, and in forming basic salts. The bromide is white, the iodide yellow.

424. **Lead Sulphate, $PbSO_4$**, is one of the most insoluble of the lead salts; it dissolves readily in caustic alkalies, and slightly in moderately concentrated sulphuric acid, but separates out again when the acid is diluted to any great extent. Lead sulphate dissolves somewhat readily in hot and moderately concentrated hydrochloric acid. If the solution be cooled, however, crystals of lead chloride are deposited.

425. **Lead Nitrate, $Pb(NO_3)_2$**, is obtained in white crystals by dissolving the metal or its oxide or carbonate in dilute nitric acid, and concentrating the solution until on cooling it crystallizes. The crystals crackle somewhat violently on heating, giving off oxygen and nitrogen peroxide, and leaving a residue of litharge.

426. **Lead Carbonate, $PbCO_3$.**—When sodium carbonate is added to a solution of lead nitrate basic carbonates of variable composition are precipitated. Normal lead carbonate can, however, be obtained by passing carbon dioxide into a dilute solution of lead acetate (sugar of lead).

The basic carbonate known as "white lead" is of great importance in consequence of its application as a white pigment. If a solution of lead acetate be boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon dioxide through the solution a white precipitate of this basic carbonate, essentially $(PbCO_3)_2.Pb(OH)_2$. is deposited.

Exp. 211.—Prepare a solution of basic lead acetate and from this "white lead" by the method just described.

Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the *Dutch process.* In this process coils of sheet lead are placed in conical vessels (Fig. 92) resting on a ledge, the bottom of the vessel containing weak acetic acid. These vessels are about 8 inches high, and a large number of them are then stacked together in layers, each layer being covered with tan or other fermenting vegetable matter. The stacks are very large, say 15 ft. square by 20 ft. high, and the heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with the lead. The acetic acid in conjunction with the oxygen of the air slowly attacks the lead with formation of basic lead acetate, $Pb(C_2H_3O_2)_2.Pb(OH)_2$, according to the equation—

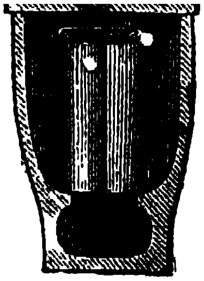
FIG. 92.

$$2\ Pb + O_2 + 2\ H.C_2H_3O_2 = Pb(C_2H_3O_2)_2.\ Pb(OH)_2.$$

As soon as it is formed, however, the basic acetate is acted upon by the carbon dioxide produced during the fermentation, with formation of basic lead carbonate, $(PbCO_3)_2$. $Pb(OH)_2$ (white lead) and free acetic acid (water also entering into the reaction)—

$$3\,[Pb(C_2H_3O_2)_2.\,Pb(OH)_2] + 4\,CO_2 + 2\,H_2O = 2\,[(PbCO_3)_2.Pb(OH)_2] + 6\,H.C_2H_3O_2.$$

This equation does not, however, represent the whole of the change which takes place, for some normal acetate is formed thus—

$$3\,[Pb(C_2H_3O_2)_2.\,Pb(OH)_2] + 2\,CO_2 = (PbCO_3)_2.\,Pb(OH)_2 + 3\,Pb(C_2H_3O_2)_2 + 2\,H_2O.$$

The free acetic attacks more lead as in the first equation, and so the cycle of changes is repeated. The normal acetate in the presence of air and water also acts upon the lead with formation of the basic acetate—

$$2\,Pb(C_2H_3O_2)_2 + O_2 + 2\,Pb + 2\,H_2O = 2\,[Pb(C_2H_3O_2)_2.\,Pb(OH)_2].$$

The basic acetate is then acted upon by carbon dioxide as already described.

427. **Lead Tetracetate, $Pb(C_2H_3O_2)_4$.**—This compound is obtained by acting on red lead with acetic acid. The product is carefully filtered and the filtrate is then allowed to crystallise.

In this compound as well as in the tetrachloride we have evidence of the tetravalency of lead, a character which it shares in common with all the elements of this group, but lead possesses it in a less degree than most of the other members.

QUESTIONS.—CHAPTER XXX.

1. Describe in some detail the process of obtaining lead from galena. What other metal is frequently extracted from the lead so obtained and how is the process carried out?
2. Give an account of the behaviour of lead towards the common acids, and water. How would you examine a sample of water for dissolved lead?

3. How may the following compounds of lead be prepared from the metal:—Lead nitrate, red lead, and lead chloride? Describe briefly the properties of these substances.
4 How would you prepare metallic lead from lead sulphate? What is the behaviour of this compound towards sulphuric acid, hydrochloric acid, water, and alkalies?
5. What is white lead? Describe the processes by which this substance is manufactured, indicating by equations the probable chemical changes involved.
6. Describe how you would prepare some lead dioxide, given litharge. Compare the action of sulphuric and hydrochloric acids on lead dioxide and red lead.

CHAPTER XXXI.

IRON.

428. **Occurrence.**—In the *metallic* form iron has been found in large masses in Greenland and occurs also in meteorites associated with cobalt and nickel. As *oxides* it is found as magnetite, Fe_3O_4, in masses or octahedral crystals chiefly in Lapland, Sweden, Siberia, and some parts of North America; as hæmatite, Fe_2O_3, in Belgium, Sweden, Elba, to the south of Lake Superior, and in England it is worked in the neighbourhood of Whitehaven and Ulverston; as limonite, $2Fe_2O_3.3H_2O$, in South Wales and in Spain; the bog iron ores which occur in Ireland, Sweden, and North Germany belong to the class of hydrated oxides. The *carbonate* is known as the mineral spathic iron ore, or in the less pure and more earthy form of clay ironstone, and, associated with carbonaceous matter, as black band ironstone. Iron occurs combined with *sulphur* chiefly in the form of iron pyrites, FeS_2, which is found in large quantities in Spain, and crystallises in the regular system; the form known as marcasite crystallises in the rhombic system. Ferrous sulphide, FeS, occurs in meteorites.

429. **Metal.**—The ores employed in the production of iron on the large scale must be such as can be readily reduced and contain as little arsenic and sulphur as possible, since these elements are difficult to eliminate and have a deteriorating effect on the metal. The oxides or hydrated oxides and carbonates are the only ores which are applicable to iron smelting.

Commercial iron occurs in three forms: (1) cast iron, (2) wrought or malleable iron, (3) steel. The differences between these substances depend chiefly on the amount of carbon they contain. In practically all cases the ore is first converted into cast iron (or pig iron), and the other forms are obtained from the latter.

430. **Production of Cast Iron.**—The ore (if clay ironstone or a spathic ore) is first calcined and then subjected to the operation of smelting in a blast furnace.

The *calcination* is performed by stacking the ore, with a small quantity of fuel, in heaps (or in shallow kilns), and carefully regulating the temperature and air supply so that—(*a*) Most of the moisture, carbon dioxide, sulphur, and arsenic are expelled. (*b*) The ferrous oxide undergoes sufficient oxidation to ferric oxide to avoid the production of ferrous silicate during the smelting operation. (*c*) The ore is rendered more porous, a condition which facilitates its ultimate reduction to metallic iron.

The calcining operation is thus not only essential for getting rid of certain objectionable impurities, but also relieves the work of the blast furnace.

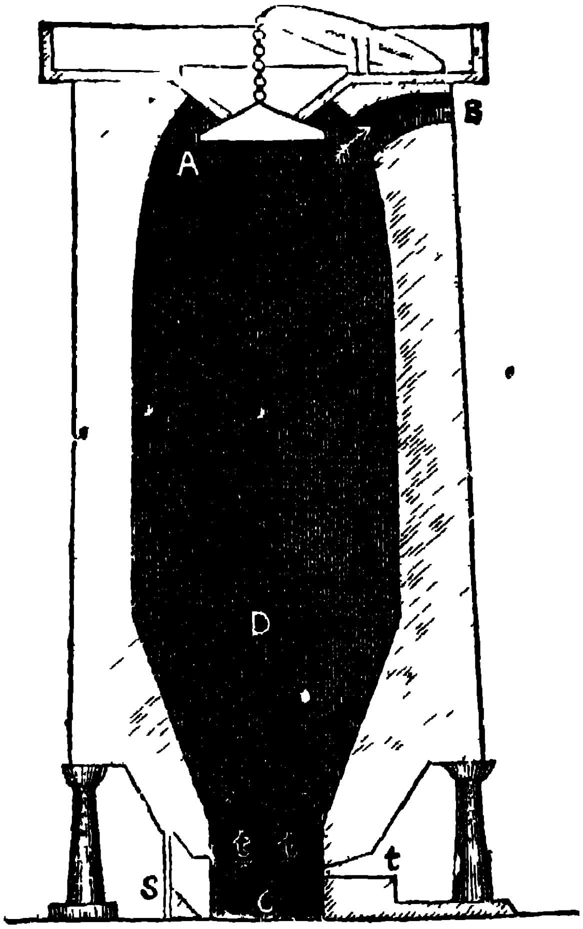

Fig. 93.

The *smelting* is performed in a tall furnace known as the blast furnace, the form of which will be seen by reference to Fig. 93. The height of such a furnace may be as much as 80 ft. and its greatest internal width 25 ft. (viz. at the "boshes" D). The mouth of the furnace is closed by a "cup and cone," as shown at A, and the waste gases arising from it pass away by a pipe which is shown at B, just below the mouth. In its lower part the furnace gradually narrows below the boshes and at its base is the "hearth" C, a space about 8 ft. in diameter and the same in height.

There is an outlet for the slag at S, just above the "dam" in the "fore hearth," which is shown in the figure just to the left of the hearth proper. Below this, the iron is tapped off at intervals of about 12 hours. The charge in such a furnace consists of 4 parts calcined ironstone to 1 part of limestone with coke equal to somewhat less than half the weight of the ironstone, though the proportions vary in some degree according to circumstances, such as the nature of the ore and the character of the pig iron to be produced. The air is introduced under forced blast at openings, near the base of the furnace, by water-jacketed twyers, t t t, 5 tons (or about 5000 cubic yards) of air and $2\frac{1}{2}$ tons of calcined ore being required per ton of iron produced.

This quantity of air, large as it seems, is insufficient for the complete oxidation of the carbon, and the gases escaping from the furnace consist largely of carbon monoxide and nitrogen. They are led off by the pipe previously referred to and furnish the means of heating the air supplied to the furnace; this effects an economy of fuel and also conduces to the attainment of a high and equal temperature in the furnace. The process goes on continuously for years, until indeed the furnace must be blown out for repairs, and fresh quantities of the charge are periodically introduced by lowering the cone at the mouth of the furnace.

The temperature and the composition of the materials in the furnace of course vary at different parts. The temperature of the charge in the upper zone does not exceed dull red heat, and lower down increases until near the base of the furnace a white heat (over 2000° C.) prevails.

431. Chemical Changes which take place in the Blast Furnace.—The first change which takes place is the combination of the oxygen of the air-blast with the carbon of the coke to form carbon dioxide.

$$C + O_2 = CO_2 \quad . \; . \; . \; . \; . \quad (i)$$

As the carbon dioxide passes up the furnace over the hot carbon it undergoes reduction to the carbon monoxide.

$$CO_2 + C = 2\,CO \quad . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

The temperature of the charge gradually rises as it descends the furnace, and at a certain point it reaches the temperature (a dull red heat) at which the ascending carbon monoxide is able to reduce the ferric oxide to metallic iron. The reduction probably takes place in two stages, ferrous oxide being formed as an intermediate product—

$$Fe_2O_3 + CO = 2\,FeO + CO_2 \quad . \; . \; . \; . \; . \quad \text{(iii)}$$

$$FeO + CO = Fe + CO_2 \quad . \; . \; . \; . \; . \quad \text{(iv)}$$

These two changes take place chiefly in the upper zone, the temperature being 600° to 900° C. The reduction of the iron oxide is, however, not complete, for iron is able to reduce both carbon dioxide and carbon monoxide at high temperature—

$$2\,Fe + 3\,CO_2 = Fe_2O_3 + 3\,CO \quad . \; . \; . \; . \; . \quad \text{(v)}$$

$$2\,Fe + 3\,CO = Fe_2O_3 + 3\,C \quad . \; . \; . \; . \; . \quad \text{(vi)}$$

and these reactions also take place to some extent.

Another change which is brought about in the upper zone is the decomposition of limestone into lime and carbon dioxide—

$$CaCO_3 = CaO + CO_2 \quad . \; . \; . \; . \; . \quad \text{(vii)}$$

As we approach the middle of the furnace the temperature becomes sufficiently high (1000° C.) to bring about some decomposition of carbon monoxide with separation of carbon—

$$2\,CO = CO_2 + C \quad . \; . \; . \; . \; . \quad \text{(viii)}$$

The small quantity of iron oxide still present in the iron when it reaches this zone now undergoes reduction chiefly by the action of free carbon—

$$Fe_2O_3 + 3\,C = 2\,Fe + 3\,CO \quad . \; . \; . \; . \quad \text{(ix)}$$

i.e. we have a reversal of reaction (vi).

At this stage the iron is in a spongy condition, the temperature being insufficient to melt it. As it passes down into the hotter parts of the furnace it takes up carbon in considerable quantity. The melting point of the iron is thereby lowered, and this fact combined with the increase in temperature results in the metal becoming completely melted. The molten iron collects in the hearth of the furnace

Iron takes up several other elements in addition to carbon at various stages of its descent through the furnace, viz.: sulphur, phosphorus, and silicon. These are absorbed in the order named, *i.e.* sulphur at the lowest temperature and silicon at the highest. They are derived from compounds present in the ore or in the limestone. Manganese is also very frequently present in iron in small quantity.

We have yet to mention the formation of the *slag*. When the lime produced in the upper zone by the decomposition of limestone reaches the lower and hotter zone, it combines with the siliceous matters present in the ore to produce a readily fusible slag consisting mainly of calcium and aluminium silicates. Since the molten slag has a smaller specific gravity than the iron, it collects above the metal, and as the process goes on it flows away through the slag hole.

When a sufficient amount of metal has accumulated, it is run off and cast in open furrows of sand in "pigs" about 3 ft. long and 3 to 4 inches thick.

432. **White pig** is fine-grained and contains 3 to 4 per cent. of carbon, chiefly in combination with the iron as iron carbide; if treated with dilute hydrochloric acid it dissolves almost completely, evolving gaseous hydrocarbons, the presence of which is rendered evident by their unpleasant odour. *Grey pig* is coarse-grained, and when freshly fractured crystals of graphite are visible to the naked eye; the amount of carbon present does not differ essentially from that in white pig, but it is chiefly in the graphitic form and is not acted upon by dilute acid. Such pig iron when heated with dilute acid leaves therefore a

residue consisting of carbon. There is also an intermediate form known as "*Mottled pig.*"

Exp. 212.—Dissolve in concentrated HCl fragments of (*a*) white pig iron, (*b*) grey pig iron, noting differences in the residues and in the gas evolved in each case.

In addition to carbon, pig iron contains smaller quantities of silicon (about 2 per cent.), phosphorus (about 0·7 per cent.), and sulphur (about 0·1 per cent.). *Spiegeleisen* or *specular iron* is a variety of pig iron obtained from manganiferous ores. Besides manganese, it contains more combined carbon than ordinary pig iron (3·5 to 6 per cent.). Spiegeleisen is largely used in the manufacture of Bessemer steel (*q.v.*).

433. **Production of Wrought Iron.**—Wrought iron as a commercial product is essentially iron containing only a minimum quantity of impurities, amounting in all to about 0·5 per cent. The removal of carbon, sulphur, etc., is effected by first "puddling" the pig iron, a process in which the latter is heated in contact with ferric oxide in presence of air, and then hammering and rolling it whilst hot, the mechanical pressure serving to develop a fibrous texture and to squeeze out slag and other matters retained by the iron.

434. **Production of Steel.**—Steel consists of iron associated with from 0·3 to 1·5 per cent. of carbon. In the *Bessemer Process* cast iron is converted into *steel* by introducing the molten metal into a large pear-shaped steel vessel (called a *converter*) lined with suitable material to withstand the high temperature, and blowing air through till the impurities are oxidised.

A quantity of carbon in the form of *spiegeleisen* is now added, which is considerably less than that originally present in the cast iron.

Other processes are also used for the conversion of cast iron into steel, but it is not necessary for us to consider them here.

435. Composition of Wrought Iron, Cast Iron, and Steel.—The following table shows the general composition of these products:—

	Wrought Iron.	Steel.	Cast Iron.
Iron	99·5	98·5	92 to 95
Carbon	0·1 to 0·3	0·3 to 1·5	1·5 to 4·5
Sulphur	trace	0·04	0·1
Phosphorus ...	0·2	0·03 to 0·1	0·5
Silicon	nil	0·2	1 to 4
Manganese ...	nil	0 to 1 or more	nil

436. Properties of Iron and Steel.—The properties of *wrought iron*, *cast iron*, and *steel* differ considerably. This difference depends chiefly upon the quantity of carbon present. *Wrought iron*, which is nearly pure iron, is a soft, grey, malleable metal possessing considerable tensile strength (*i.e.* a heavy weight can be hung on to a tolerably thin iron wire without breaking it). As the percentage of carbon increases, the iron becomes harder and less malleable; up to a certain point the tensile strength increases, but beyond this it diminishes. *Cast iron*, which contains the highest percentage of carbon, is very brittle, and its tensile strength is much smaller than that of wrought iron.

Steel is very tough, possessing even greater tenacity than wrought iron, and it possesses the remarkable property of becoming very hard on being heated up and then suddenly cooled. If it is now heated again to a moderate temperature it becomes softer, and by varying the temperature the hardness can be regulated. This process is called "tempering," and the steel is said to "take a temper"; wrought iron and cast iron cannot be tempered.

The melting point of all three substances is very high (approximately 1600°—1900° C.), that of cast iron being the lowest and that of wrought iron the highest.

All three forms are unacted upon by dry air at ordinary temperatures, but in moist air they become coated with *iron rust*, which consists chiefly of hydrated ferric oxide. Rusting is greatly accelerated by the presence of carbon dioxide or acid vapours.

437. Uses of Iron and Steel.—*Wrought iron* was formerly used for a great variety of purposes, but steel has now taken its place to a very large extent. The greater part of the wrought iron manufactured at the present time is employed for making the cores of electromagnets used in dynamos and electric motors. A considerable amount is also employed by the blacksmith, who requires a metal which can be easily worked at a red heat; horseshoes, for instance, are made of wrought iron.

Cast iron is, as its name implies, used for *castings*—*e.g.* fire-grates, fly-wheels, and pistons; its value for this purpose depends upon (1) its low melting-point compared with wrought iron and steel; (2) the fact that on cooling from a temperature somewhat above the melting-point a considerable expansion takes place which enables the molten metal to fill every part of a mould into which it is poured.

The purposes for which *steel* is employed are innumerable: it is used for making tools, guns, armour-plating for ships, boiler-plates, rails, girders for bridges, etc., etc.

438. Pure Iron.—The purest form of commercial iron is piano-wire, which contains about 99·7 per cent. of iron. To obtain still more pure iron, ferrous oxide, oxalate, or chloride may be reduced by heating them in a current of hydrogen. If the reduction is carried out at a comparatively low temperature, the iron is obtained as a fine black powder which oxidises so readily that it becomes incandescent on exposure to air. This is termed "pyrophoric iron." When reduced at a higher temperature iron is not pyrophoric. Pure iron may also be deposited by electrolysis from a solution of ferrous sulphate.

439. Action of Acids on Iron.—The action of the three common mineral acids on iron is as follows:—

Hydrochloric acid, whether dilute or concentrated, gives hydrogen and ferrous chloride, $FeCl_2$.

Sulphuric acid when dilute gives hydrogen and ferrous sulphate, $FeSO_4$. The concentrated acid has no action in the cold, but on heating the metal dissolves with liberation of sulphur dioxide and formation of ferric sulphate, $Fe_2(SO_4(_3$, and ferrous sulphate.

Nitric acid, whether dilute or concentrated, readily dissolves iron with formation of brown fumes, which are very copious in the latter case. With the dilute acid, nitrogen peroxide, nitric oxide, nitrous oxide, and free nitrogen are all evolved in varying quantities, and the solution contains ammonium nitrate, ferrous nitrate ($Fe(NO_3)_2$), and ferric nitrate ($Fe(NO_3)_3$). The chief products when the concentrated acid is used are nitrogen peroxide, nitric oxide, and ferric nitrate.

It is found, however, that *pure* concentrated nitric acid does not dissolve iron which becomes "passive." In this condition it is not acted upon by other acids, nor does it, like ordinary iron, precipitate copper from a solution of copper sulphate. The "passive" state of iron has been attributed to various causes, but the most probable explanation is the formation of a film of magnetic oxide, as it has been shown that iron can be made passive by heating in oxygen.

440. **Oxides and Hydroxides.**—Three oxides of iron are known to exist in the free state, viz. ferrous oxide, FeO, magnetic oxide, Fe_3O_4, and the sesquioxide or ferric oxide, Fe_2O_3, whilst a fourth (probably FeO_3) occurs in combination in certain unstable salts, the ferrates of the alkalies and alkaline earths.

Ferrous Oxide, FeO, is obtained by reduction of the sesquioxide in hydrogen at 300° C. or by heating the oxalate with the exclusion of the air or oxygen. It glows on exposure to air at ordinary temperatures, and readily becomes oxidised to ferric oxide. The *ferrous hydroxide* $Fe(OH)_2$, a white flocculent substance obtained by precipitation of ferrous salts with potash, oxygen being rigidly excluded, also absorbs oxygen with great avidity, turning dark green and ultimately passing into reddish-brown ferric hydroxide, $Fe(OH)_3$. Ferrous oxide is a basic oxide, and by the action of the several acids upon it (or upon metallic iron) a series of salts known as the *ferrous* *salts* are obtained. These salts are usually white in the anhydrous condition and pale green when in the hydrated form.

441. **Ferric Oxide (Sesquioxide), Fe_2O_3,** occurs in considerable deposits either as such or associated with water of hydration. (See § 428.) It is obtained as a residue when ferrous sulphate is strongly heated, and this residue is employed as a polishing powder and as a pigment, yielding yellow, red, or brown ochre. Iron rust consists chiefly of hydrated ferric oxide. The *hydroxide*, $Fe(OH)_3$, is obtained on precipitating ferric salts with alkalies—

$$FeCl_3 + 3\,KOH = Fe(OH)_3 + 3\,KCl.$$

It forms the base of the *ferric salts*.

442. **Magnetic Oxide of Iron, Fe_3O_4,** occurs as magnetite or lodestone, and is formed when metallic iron is strongly heated in steam or carbon dioxide. It may be conveniently prepared as follows:—

Exp. 213.—Weigh out 2 grammes of ferrous sulphate crystals, dissolve in water, acidify with sulphuric acid, add some nitric acid, and boil till brown fumes cease to be evolved even on the addition of a few more drops of nitric acid. Now add caustic potash to the solution till a precipitate begins to form* and *just* redissolve this with dilute sulphuric acid.

Next weigh out 1 gramme of ferrous sulphate crystals, dissolve in water, and add the solution to that just prepared. Shake up in order to mix thoroughly and then add caustic potash. Filter off the black precipitate which forms, wash it, and dry on the water-bath.

The changes which have taken place are as follow:—The ferrous sulphate when boiled with nitric acid was oxidised to ferric sulphate. The ferric sulphate formed was equivalent to *two* grammes of ferrous sulphate, and *one* gramme of ferrous sulphate was subsequently added, so that the solution to which caustic potash was added contained equal numbers of molecules of ferrous and ferric sulphates, (since each molecule of ferric sulphate is formed from two molecules of ferrous sulphate—see equation in § 203).

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* The object of this is to neutralise the excess of nitric acid so that it does not oxidise the ferrous sulphate subsequently added.

The effect of adding caustic potash to this solution is to produce a black precipitate, which may be considered as a compound of equal numbers of molecules of ferrous and ferric hydroxides, and this compound when dried on the water-bath loses water, and is converted into magnetic oxide of iron, which may be considered as a compound of one molecule of ferrous oxide and one molecule of ferric oxide.

One molecule of ferrous oxide = FeO
„ „ „ ferric oxide = $\underline{Fe_2O_3}$
„ „ „ magnetic oxide of iron = $\underline{\underline{Fe_3O_4}}$

$$FeSO_4 + Fe_2(SO_4)_3 + 8\ KOH = Fe_3(OH)_8 + 4\ K_2SO_4,$$
$$Fe_3(OH)_8 = Fe_3O_4 + 4\ H_2O.$$

This oxide of iron derives its name from the fact of its being magnetic. Strong mineral acids act upon it, forming a mixture of ferrous and ferric salts, and no series of salts corresponding to it has been prepared.

443. **Ferrous Sulphide, FeS,** is prepared by heating together iron filings and sulphur, or by the reduction of ferrous sulphate by carbon. The precipitated form of it, obtained by adding an alkaline sulphide to a ferrous salt, rapidly undergoes oxidation to ferrous sulphate when exposed to air. Mineral acids act very readily on ferrous sulphide, liberating sulphuretted hydrogen. (See § 217.)

Iron Pyrites, FeS_2, is found native as iron pyrites and as marcasite; in contact with moisture and air these become slowly oxidised to ferrous sulphate. When they are heated sulphur is given off, and in presence of air this undergoes a more or less complete oxidation to sulphur dioxide, ferric oxide being left as a residue. (§ 232.)

444. Ferrous Chloride, $FeCl_2$, is obtained anhydrous in white feathery crystals by heating metallic iron in a current of dry hydrogen chloride. An apparatus similar to that represented in Fig. 94 may be employed. A spiral of fine wire is heated in a rather wide tube A, provided with a bulb B. A current of dry HCl is passed over it, and crystals of $FeCl_2$ are deposited in the bulb, from which they may be shaken out when the operation is at an end. It is deliquescent and readily soluble in water. Green crystals having the composition $FeCl_2 . 4\,H_2O$ separate out when iron is dissolved in hydrochloric acid and the solution is concentrated by evaporation. By treating such a solution with chlorine, the ferrous chloride passes into ferric chloride. The vapour of ferrous chloride at temperature between 1200° and 1500° C. corresponds to the formula $FeCl_2$.

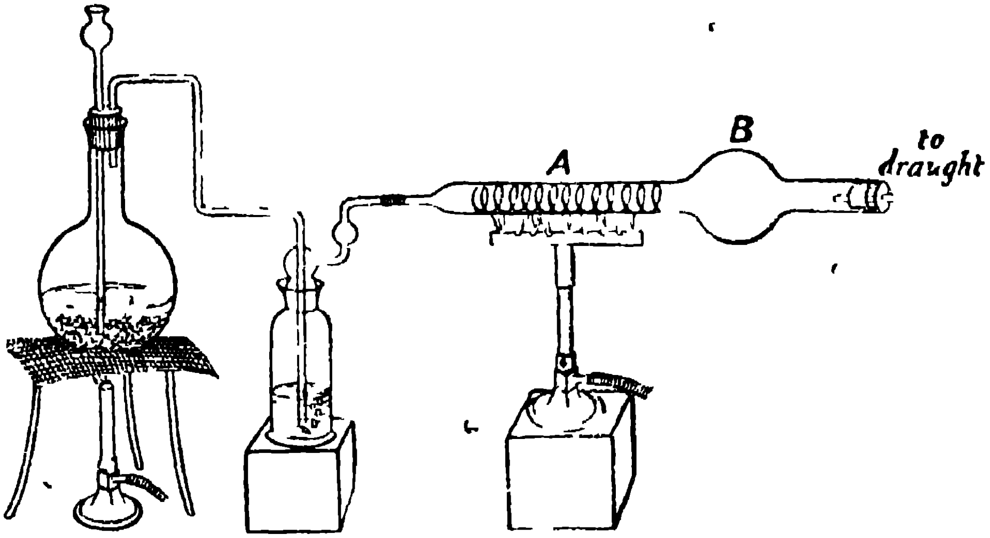

FIG. 94.

Exp. 214.—Prepare anhydrous ferrous chloride as described above. The wash-bottle shown in Fig. 94 contains strong sulphuric acid to dry the HCl. Displace the air from a small flask by CO_2. Now introduce the ferrous chloride and a little well-boiled water into the flask and quickly cork up. Shake up to bring the $FeCl_2$ into solution. On cooling, crystals of the hydrated salt separate out. It is necessary to completely remove air from the apparatus, owing to the rapidity with which $FeCl_2$ becomes oxidised. Expose a little of the solution of ferrous chloride to the air and note what takes place

445. Ferric Chloride, $FeCl_3$.—This salt is obtained in the anhydrous condition in nearly black crystals by direct union of iron and chlorine in an apparatus similar to that described in the preceding paragraph for the preparation of $FeCl_2$.

These crystals are very deliquescent and dissolve readily in water, forming a brown solution which becomes yellow on dilution. The same solution may be obtained by dissolving ferric oxide in hot concentrated hydrochloric acid, or ferric hydroxide in the dilute (or concentrated) acid; also by passing chlorine into a solution of ferrous chloride.

$$Fe_2O_3 + 6\,HCl = 2\,FeCl_3 + 3\,H_2O.$$

$$Fe(OH)_3 + 3\,HCl = FeCl_3 + 3\,H_2O.$$

$$2\,FeCl_2 + Cl_2 = 2\,FeCl_3.$$

From the solution of ferric chloride several brown crystalline hydrated salts have been obtained by varying the conditions under which the crystals separate; the compound containing the greatest amount of water of crystallisation is represented by the formula $FeCl_3, 6\,H_2O$.

Anhydrous ferric chloride can be volatilised without decomposition, its boiling point being about 280° C.; up to a temperature of over 400° C. the density of its vapour is in agreement with the composition Fe_2Cl_6, but at higher temperatures it diminishes, and at 750° C. its value is approximately halved, corresponding to the composition $FeCl_3$—

V.D. at 448° =	10·49	V.D. at 750° =	5·39
„ 518° =	9·57	„ 1050° =	5·31
„ 606° =	8·38	„ 1300° =	5·12

Fe_2Cl_6 requires 11·2 (air = 1)
$FeCl_3$ „ 5·6 („)

Exp. 215.—Prepare anhydrous ferric chloride by the method given above. Dissolve this in water and obtain crystals of the hydrated salt. Also prepare the hydrated salt by passing chlorine into a solution of ferrous chloride obtained as in Exp. 214, or by dissolving iron in hydrochloric acid.

446. Ferrous Sulphate, $FeSO_4 . 7\,H_2O$, known also as green vitriol, forms green monoclinic crystals, and is obtained by dissolving metallic iron in dilute sulphuric acid (excluding air or oxygen) and then concentrating the solution to the point at which it crystallises. It is also formed slowly by the oxidation of the mineral marcasite or iron pyrites (FeS_2) at ordinary temperatures, and is manufactured on the large scale in this way. When this salt is mixed in solution with alkaline sulphates, and sufficiently concentrated, crystals of a double salt having the composition $M_2SO_4 . FeSO_4 . 6\,H_2O$ separate out.

Ferrous salts in presence of oxidising agents, such as acidulated solutions of potassium permanganate and potassium bichromate, are converted into ferric salts, and if the amount of the oxidising agent so used is known, this reaction may be employed for estimating the iron present. Conversely, a solution of ferrous sulphate or of the double salt ferrous ammonium sulphate, of known strength, may be employed for estimating the amount of an oxidising agent present. For volumetric work ferrous ammonium sulphate is preferable to ferrous sulphate, as the former is much less readily oxidised by air.

A cold concentrated solution of ferrous sulphate dissolves nitric oxide forming $2\,(FeSO_4) . NO$, and the dark brown ring observed in testing for the presence of nitric acid (§ 194) is due to the presence of this body.

When heated in closed vessels ferrous sulphate decomposes, giving "Nordhausen" sulphuric acid ($H_2S_2O_7$), and leaving a residue of red ferric oxide.

Ferrous Ammonium Sulphate, $(NH_4)_2SO_4 . FeSO_4 . 6\,H_2O$, is formed as above described when concentrated solutions of ferrous sulphate and ammonium sulphate are mixed and the resulting solution allowed to crystallise. It forms greenish-blue crystals, which are very stable in air. This substance contains exactly one-seventh of its weight of iron, and is much employed, as already stated, in volumetric analysis.

447. Ferric Sulphate, $Fe_2(SO_4)_3$.—When ferrous sulphate is exposed to moist air it is slowly transformed into ferric sulphate, and this change (see above) is effected more rapidly in solution in presence of oxidising agents such as chlorine and nitric acid. Ferric sulphate is formed directly by dissolving ferric oxide (Fe_2O_3) in sulphuric acid.

Iron Alums.—In combination with alkaline sulphates ferric sulphate forms alums which crystallise in the same form as ordinary alum; thus iron ammonium alum has the composition $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, and differs from ordinary ammonia alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$, in the replacement of aluminium by iron. It forms octahedral crystals which have a violet tinge, and are readily soluble in water.

Exp. 216.—Prepare iron ammonium alum by mixing equivalent quantities of ferric sulphate and ammonium sulphate, and crystallising.

The ferric sulphate is obtained by oxidising ferrous sulphate in presence of the required amount of sulphuric acid, by means of nitric acid, evaporating nearly to dryness to drive off HNO_3, and then diluting with water.

448. **Ferrous Nitrate, $Fe(NO_3)_2$, and Ferric Nitrate, $Fe(NO_3)_3$,** are prepared by the action of nitric acid on iron, the ferrous salt being obtained when cold dilute nitric acid is employed, and the ferric salt when excess of concentrated acid is added.

The ferric nitrate obtained in this way, or the product obtained by the action of nitric acid on ferrous sulphate, is used as a mordant in dyeing.

449. **Ferrous Carbonate, $FeCO_3$,** occurs, as already stated, as a mineral product, spathic iron ore. It is formed when an alkaline carbonate is added to a solution of a ferrous salt. In this form it is very unstable and readily parts with carbon dioxide; the ferrous hydroxide thus produced then undergoes oxidation to ferric hydroxide, and the reddish-brown deposit which is found in chalybeate waters is no doubt formed from ferrous carbonate in this way.

QUESTIONS.—CHAPTER XXXI.

1. Give the common names, chemical names and formulae of the naturally occurring compounds of iron, and indicate their importance as ores.
2. Write an account of the preparation of pig iron. How is this transformed into (*a*) wrought iron, (*b*) steel?
3. Describe the physical properties of wrought iron, cast iron, and steel. How is the purest commercial wrought iron obtained?
4. From a sample of piano-wire how would you prepare the several oxides of iron? Describe the appearance and chemical and physical properties of these bodies.
5. How is ferrous sulphide prepared? Compare it with the disulphide. How do these substances behave towards heat and acids?
6. Describe the preparation of the chlorides of iron in the anhydrous state, giving a sketch of the apparatus you would employ. How can the two chlorides be transformed the one into the other?
7. Describe a convenient method of preparing ferrous sulphate in a state of purity. What happens to this substance (*a*) when left exposed to air, (*b*) when heated in a closed vessel, (*c*) when warmed with nitric acid, (*d*) when nitric oxide is passed into a solution of the salt?
8. How would you prepare a sample of pure ferrous ammonium sulphate? Show that this substance contains just one-seventh its weight of iron. What use is made of the compound in analysis, and on what properties does this use depend?

CHAPTER XXXII.

MODES OF FORMATION OF SALTS.

450. Many examples of the various ways in which salts are formed have been given in the foregoing pages. We shall now collect these methods together and classify them.

451. **Method 1. Direct Union of a Metal and a Non-Metal.**—This method is largely employed for the production of the anhydrous salts of the halogen acids, since most metals unite directly with the halogens. When the metal forms two salts, one containing a higher percentage of halogen than the other, it depends upon the relative masses of the metal and the halogen which react, whether the higher or the lower salt is formed. Iron, for instance, yields ferr*ic* chloride ($FeCl_3$) with excess of chlorine; but if the iron is in excess, ferr*ous* chloride ($FeCl_2$) is formed—

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3.$$
$$Fe + Cl_2 = FeCl_2.$$

Similarly, tin yields stannic chloride ($SnCl_4$) or stannous chloride ($SnCl_2$), according as chlorine or the metal is in excess—

$$Sn + 2\,Cl_2 = SnCl_4.$$
$$Sn + Cl_2 = SnCl_2.$$

The combination of mercury and iodine affords another example, HgI_2 or Hg_2I_2 being formed according as iodine or mercury is in excess.

Many sulphides can also be readily obtained by the direct union of metals with sulphur (see Exps. 64, 147).

452. Method 2. Interaction of Metals and Acids.—When acids act on metals, a salt of the metal is almost invariably obtained as one of the products. In some cases, *e.g.* when dilute hydrochloric, dilute sulphuric, or acetic acid acts on magnesium, zinc, or iron, hydrogen is the only other product, and these reactions are used in the preparation of hydrogen, as we have seen. In other cases the reactions are more complex, and these have been fully discussed in the foregoing chapters.

The action of a haloid acid on a metal always results in the formation of its *lower* salt when it forms more than one. Thus, with hydrochloric acid, iron forms ferrous chloride, $FeCl_2$, and with tin it forms stannous chloride, $SnCl_2$. We should expect this because the nascent hydrogen which is liberated in the reaction is a strong reducing agent, and would immediately reduce the higher salt if any were formed.

When the acid is a strong oxidising agent, *e.g.* nitric acid, the nascent hydrogen which may be supposed to be liberated at first is immediately oxidised to water, and it depends upon the relative masses of the metal and the acid whether the lower or the higher salt is formed. This may be illustrated by the following experiments:—

Exp. 217.—Warm a small quantity of mercury with excess of nitric acid till the metal has dissolved. Now add hydrochloric acid to the solution; no precipitate will be formed, proving the absence of any mercur*ous* nitrate (which with hydrochloric acid would form a white precipitate of mercurous chloride). The mercury has been entirely converted into mercur*ic* nitrate.

Exp. 218.—Next allow some mercury to remain in contact with about half its volume of dilute nitric acid for some time. Pour off the supernatant liquid from the mercury and add hydrochloric acid; a white precipitate is at once formed, showing that when the mercury is in excess of the acid, it is converted into mercur*ous* nitrate.

Salts of the haloid acids may be obtained by acting on a metal with either the gaseous acid or its aqueous solution; if the anhydrous salt is required, only the former method can be employed in many cases, because, on evaporating the aqueous solution of the salt to dryness and igniting to drive off water, the salt and the water react on each other with formation of the halogen acid and the oxide of the metal. Ferric chloride, for instance, is decomposed by water on evaporation to dryness and igniting, with formation of ferric oxide and hydrogen chloride—

$$2FeCl_3 + 3H_2O = Fe_2O_3 + 6HCl.$$

Exp. 219.—Evaporate some ferric chloride solution to dryness and ignite. Notice the evolution of acid fumes (hydrogen chloride). When these cease to come off allow the residue to cool, and then try to dissolve it in water: it is insoluble (whereas ferric chloride is soluble).

453. **Method 3. Interaction of a Metal with a Salt of another Metal.**—In general one metal will displace another from its salts when the oxide of the former is more strongly basic than that of the latter, *i.e.* the oxide reacts more readily with acids. Thus iron displaces copper from a solution of copper sulphate (as we saw in Exp. 1), and zinc displaces silver from a solution of silver nitrate—

$$\begin{aligned} Fe + CuSO_4 &= Cu + FeSO_4. \\ Zn + 2AgNO_3 &= 2Ag + Zn(NO_3)_2. \end{aligned}$$

454. **Method 4. Direct Union of a Basic Oxide and an Acidic Oxide.**—Many basic oxides combine directly with acidic oxides to form salts. For example, when barium oxide, BaO, and sulphur trioxide, SO_3, are mixed together they combine to form barium sulphate with such energy that the mass becomes red-hot—

$$BaO + SO_3 = BaSO_4.$$

Again, quicklime and carbon dioxide readily unite to form calcium carbonate—

$$CaO + CO_2 = CaCO_3.$$

455. **Method 5. Interaction of Bases and Acids.**—This is the most general method. It has been fully discussed and illustrated in the foregoing chapters.

456. **Method 6. Interaction of an Acid with a Salt of a Weak Acid.**—The chief examples of this method consist of the preparation of salts by the action of acids on *carbonates.*

Exp. 220.—Add chalk, a little at a time, to some dilute nitric acid contained in a beaker till the further addition ceases to cause effervescence. Filter and evaporate the filtrate to dryness in a porcelain dish. The white residue is *calcium nitrate.*

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

457. **Method 7. Interaction of an Acid with a Salt of a more Volatile Acid.**—An example of this method is the conversion of a nitrate into a sulphate by heating with strong sulphuric acid. The volatile nitric acid is driven off, leaving the salt of the much less volatile sulphuric acid behind.

Thus when potassium nitrate is gently heated with sulphuric acid, potassium hydrogen sulphate is formed—

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Another example is the conversion of sodium chloride into the sulphates of sodium. (See § 351.)

458. **Method 8. Interaction of a Base with a Salt of a more Volatile Base.**—When caustic potash or soda is heated with an ammonium salt, the volatile base, ammonia, is driven off and the corresponding potassium salt remains—

$$2KOH + (NH_4)_2SO_4 = K_2SO_4 + 2NH_3 + 2H_2O.$$

459. **Method 9. Interaction of a Base with a Salt of an Insoluble Base.**—The majority of the hydroxides of the metals are insoluble in water. If, then, a solution of a soluble base such as caustic potash or soda is added to a salt of a metal which forms an insoluble hydroxide, double decomposition takes place with precipitation of the insoluble hydroxide and formation of a salt of potassium or sodium; for it is observed that, *when an insoluble substance can be formed by double decomposition, that substance is*

usually formed. For example, on adding caustic potash to a solution of copper sulphate, $CuSO_4$, cupric hydroxide, $Cu(OH)_2$, is precipitated, and potassium sulphate, K_2SO_4, goes into solution—

$$2KOH + CuSO_4 = Cu(OH)_2 + K_2SO_4.$$

The cupric hydroxide can be separated from the potassium sulphate by filtration.

460. **Method 10. Interaction of Two Salts.**—Representing the double decomposition between two salts by the equation—

$$A + B = C + D,$$

this method of preparation can be used for a salt, C, when that salt is less soluble or more volatile than A, B, or D. For example, silver chloride, $AgCl$, is insoluble in water, whereas silver nitrate, $AgNO_3$, potassium chloride, KCl, and potassium nitrate, KNO_3, are all soluble. We can therefore prepare silver chloride by mixing solutions of silver nitrate and potassium chloride; silver chloride is precipitated and may be separated from the soluble salts by filtration—

$$AgNO_3 + KCl = AgCl + KNO_3.$$

Again, mercuric chloride, $HgCl_2$, is volatile, whilst sodium chloride, sodium sulphate, Na_2SO_4, and mercuric sulphate, $HgSO_4$, are non-volatile. If, therefore, a mixture of mercuric sulphate and sodium chloride is heated together, double decomposition takes place and mercuric chloride passes away as vapour, condensing again on a cool surface.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

461. **Method 11. Interaction of Two Bases.**—A few bases, notably the oxides and hydroxides of zinc, tin, and aluminium, are soluble in caustic potash or caustic soda solution with formation of salts. The explanation is that, in the presence of a strong base, such as caustic potash, a

substance which generally acts as a weak base may act as a weak acid. The following equations represent the formation of salts in this manner:—

$$2KOH + Zn(OH)_2 = \underset{\text{Potassium zincate (in solution only)}}{K_2ZnO_2} + 2H_2O.$$

$$2NaOH + Al_2O_3 = \underset{\text{Sodium aluminate}}{2NaAlO_2} + H_2O.$$

$$2KOH + SnO_2 = \underset{\text{Potassium stannate}}{K_2SnO_3} + H_2O.$$

462. **Method 12. Interaction of Metals with Bases.**— A few metals are soluble in potash solution with evolution of hydrogen, more especially zinc and aluminium. The salts obtained are the same as those produced when the oxides or hydroxides of the metals are used instead of the metals themselves, as in the preceding method: thus when aluminium is dissolved potassium aluminate is formed—

$$Al_2 + 2KOH + 2H_2O = \underset{\text{Potassium aluminate}}{2KAlO_2} + 3H_2.$$

Most metals are attacked slowly by fused potash, silver being the most resistant.

Of the twelve methods enumerated, the 1st, 2nd, 5th, 6th, and 9th are far the most important.

QUESTIONS.—CHAPTER XXXII.

1. Discuss the effect of mass on the nature of the products obtained by the action on metals of (1) the halogens, (2) nitric acid.
2. Why would you expect to get only the *lower* salt when a haloid acid acts on a metal which can give rise to two series of salts?
3. Why cannot anhydrous ferric chloride be obtained by evaporating the aqueous solution of the salt to dryness? How is the anhydrous salt obtained?

4. Express by equations the action of (1) barium monoxide on sulphur trioxide, (2) zinc on silver nitrate, (3) caustic potash on ammonium sulphate, (4) caustic soda on zinc hydroxide.
5. Under what conditions can a salt be conveniently prepared by the interaction of two other salts?
6. Give examples of the formation of salts from (1) two bases, (2) a metal and a base.

SECTION IV.—CHEMICAL CALCULATIONS.

CHAPTER XXXIII.

CHEMICAL CALCULATIONS.

463. **The Relations between Weight and Volume of Gases.**—From Avogadro's hypothesis it follows at once that the densities of gases are proportional to their molecular weights. In order to express the weight of any gas it is convenient to remember as the basis of calculation that *1 litre of hydrogen at the standard temperature* (0° *C.*) *and pressure* (760 *mm. of mercury*) *weighs* 0·09 *gramme*, or that 11·11 litres of hydrogen weigh one gramme.

If then we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule	of	hydrogen	is expressed by	H_2	(2)
,,	,,	nitrogen	,,	N_2	(28)
,,	,,	oxygen	,,	O_2	(32)
,,	,,	chlorine	,,	Cl_2	(71)
,,	,,	ozone	,,	O_3	(48)
,,	,,	phosphorus	,,	P_4	(124)
,,	,,	water vapour	,,	H_2O	(18)
,,	,,	hydrochloric acid	,,	HCl	(36·5)
,,	,,	carbon dioxide	,,	CO_2	(44)
,,	,,	nitric oxide	,,	NO	(30)
,,	,,	sulphide dioxide	,,	SO_2	(64)
,,	,,	sulphuretted hydrogen	,,	H_2S	(34)
,,	,,	ammonia	,,	NH_3	(17)

and so on.

The relative weights are, then, those stated in parenthesis after the symbol in the above list, as derived from the respective atomic weights.

Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or (0·09 × 14) grammes; a litre of carbon dioxide weighs (0·09 × 22) grammes; a litre of sulphuretted hydrogen weighs (0·09 × 17) grammes.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11·11 litres of hydrogen weigh 1 gramme or 22·22 litres of hydrogen weigh 2 grammes, the same number of grammes as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being *m*, 22·22 litres of any gas whatever weigh *m* grammes.

22·22	litres	of	nitrogen	weigh	28	grammes.
22·22	„	„	oxygen	„	32	„
22·22	„	„	chlorine	„	71	„
22·22	„	„	sulphur dioxide	„	64	„
22·22	„	„	ammonia	„	17	„

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given. For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example:—

(1) Required the weight of 100 c.c. of carbon dioxide at 0° C. and 760 mm. pressure—

1,000 c.c. (1 litre) of	hydrogen	weigh	0·09	grammes.
„ „	carbon dioxide	„	1·98	„
100 cubic centimetres of	„ „	„	0·198	„

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

(2) Required the volume occupied by 0·5 gramme of ammonia at 0° C. and 760 mm. pressure—

17 grammes of ammonia occupy 22·22 litres.
1 gramme " occupies 1·307 "
0·5 " " " 0·635 "

It is useful also to bear in mind that air is 14·435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of sulphur dioxide is found by experiment to be 1·53, air being the unit.

The density compared with hydrogen is therefore 1·53 × 14·435, or 22·1, a value agreeing well with that deduced from the accepted composition of this gas.

464. **Correction for Temperature and Pressure.**—We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. VIII.) that a gas at 0° C. expands $\frac{1}{273}$ of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see § 48), will be found the most useful, as a few examples will show. In order to make the calculation it is, in the first place, necessary to convert the temperatures as ordinarily stated into absolute temperatures.

(3) A litre of gas is measured at 0° C.; what volume will it occupy at − 20° C., and what at 50° C.?

0° C. = 273° absolute.
− 20° C. = 253° "
+ 50° C. = 323° "

$$\text{Volume required is at} - 20^\circ \text{C.} \quad 1 \text{ litre} \times \frac{253}{273} = 926{\cdot}8 \text{ c.c.}$$

$$\text{"} \quad \text{"} \quad \text{"} \quad + 50^\circ \text{C.} \quad 1 \text{ litre} \times \frac{323}{273} = 1183{\cdot}2 \text{ c.c.}$$

(4) The volume of a gas measured at 10° C. is found to be 150 c.c.; what volume would it occupy at the standard temperature (0° C.)?

10° C. = 283° absolute.

Volume required is at 0° C. $150 \times \frac{273}{283} = 144{\cdot}7$ c.c.

(5) The volume of a gas measured at 15° C. is found to be 250 c.c.; what volume would it occupy at – 15° C. and at 57° C. respectively?

15° C. = 288° absolute.
– 15° C. = 258° „
+ 57° C. = 330° „

$$\text{Volume required at } -15^\circ\text{C.} = 250 \times \frac{258}{288} = 224{\cdot}0 \text{ c.c.}$$

$$\text{„ „ „ } +57^\circ\text{C.} = 253 \times \frac{330}{288} = 286{\cdot}5 \text{ c.c.}$$

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see § 49), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

(6) A gas measured at standard atmospheric pressure (760 mm.) is found to occupy 1·5 litres; what volume will it occupy at 1,000 mm. and at 100 mm. pressure?

$$\text{Required volume at 1,000 mm. is } 1{,}500 \times \frac{760}{1{,}000} = 1{,}140 \text{ c.c.}$$

$$\text{„ „ „ 100 mm. is } 1{,}500 \times \frac{760}{100} = 11{,}400 \text{ c.c.}$$

(7) The volume of a gas at 500 mm. pressure is found to be 250 c.c.; what would it measure under 5 atmospheres pressure?

$$5 \text{ atmospheres} = (760 \times 5) \text{ mm.} = 3{,}800 \text{ mm.}$$

$$\text{Required volume at 5 atmos.} = 250 \times \frac{500}{3{,}800} = 32{\cdot}9 \text{ c.c.}$$

Finally, an example is given of the allowance for both temperature and pressure in the same expression.

(8) A gas occupies 190 c.c. at 13° C. and 740 mm. pressure; what volume would it occupy at standard temperature and pressure (0° C. and 760 mm.), and what at – 130° C. and 780 mm. pressure?

13° C. = 286° absolute.
0° C. = 273° „

$$\text{Volume at } 0°\text{ C. and 760 mm.} = 190 \times \frac{273 \times 740}{286 \times 760} = 176{\cdot}6 \text{ c.c.}$$

−130° C. = 143 absolute.

$$\text{Volume at } -130°\text{ C. and 780 mm.} = 190 \times \frac{143 \times 740}{286 \times 780} \text{ c.c.}$$
$$= 90{\cdot}1 \text{ c.c.}$$

465. **The Relation between Weight and Volume of Liquids.**—The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1 :—

Specific gravity of water at	0°	= 0·99987
„ „ „	2°	= 0·99997
„ „ „	4°	= 1·00000
„ „ „	10°	= 0·99975
„ „ „	15°	= 0·99916
„ „ „	20°	= 0·99826
„ „ „	25°	= 0·99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1·8 we mean that it is heavier than water in the proportion 1·8 : 1 ; if therefore 1 c.c. of water weighs 1 gramme, 1 c.c. of such a liquid will weigh 1·8 grammes.* The following examples will show how specific gravity of liquids enters into chemical problems.

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* This is not strictly accurate, since the gramme is the weight of 1 c.c. of water *at* 4° *C.* The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0·99916.

(9) What is the weight of 100 c.c. of sulphuric acid of sp. gr. 1·84?

100 c.c. of water weighs 100 grammes.
„ „ sulphuric acid of the density given „ 184 „

(10) Hydrochloric acid of sp. gr. 1·112 contains 21 per cent. by weight of gaseous hydrochloric acid; find the volume of hydrochloric acid gas in 10 c.c. of such acid.

By the method used in the previous problem 10 c.c. of hydrochloric acid will weigh 11·12 grammes.

$\frac{11{\cdot}12 \times 21}{100} = 2{\cdot}3352$ grammes, the weight of gaseous hydrochloric acid contained in it.

36·5 grammes of HCl. occupy 22·22 litres;

$$2{\cdot}3352 \text{ grammes occupy } \frac{22{\cdot}22 \times 2{\cdot}3352}{36{\cdot}5} \text{ litres}$$
$$= 1{\cdot}421 \text{ litres.}$$

466. **The Relation between Weight and Volume of Solids,** like that of liquids, is expressed in terms of water as unit. Thus, diamond is 3·5 times as heavy as water, and its sp. gr. is 3·5; the sp. gr. of graphite is 2·2, of mercury 13·6.

The weight of these bodies that occupy the same volume as 1 gramme of water (that is, 1 c.c.) is 3·5, 2·2, and 13·6 grammes respectively.

This relation is seldom necessary in chemical calculations.

467. **Calculation of the Percentage Composition of a Body.**—When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights.

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35·5 parts by weight of chlorine.

H_2O indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

CO_2 indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.* 2 × 16) parts by weight of oxygen.

P_2O_5 indicates a compound formed by the union of 62 (*i.e.* 2 × 31) parts by weight of phosphorus with 80 (*i.e.* 5 × 16) parts by weight of oxygen.

H_3PO_4 indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i.e.* 4 × 16) parts by weight of oxygen.

36·5	parts by	weight of	HCl	contain	1 pt. of	H and 35·5	pts.	of	Cl.
18	,,	,,	H_2O	,,	2 pts.	H and 16	,,	,,	O.
44	,,	,,	CO_2	,,	12 ,,	C and 32	,,	,,	O.
142	,,	,,	P_2O_5	,,	62 ,,	P and 80	,,	,,	O.
98	,,	,,	H_3PO_4	,,	3 ,,	H, 31 of P and 64 of O.			

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound.

Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } i.e. \ 11{\cdot}11;$$

$$\text{and } \frac{16 \times 100}{18} \ ,, \ \ ,, \ \text{O, } i.e. \ 88{\cdot}88;$$

and this represents the percentage composition of water.

(11) Find the percentage composition of potassium chlorate, $KClO_3$—

$$\begin{aligned} K &= 39{\cdot}1 \\ Cl &= 35{\cdot}5 \\ O_3 &= \underline{48{\cdot}0} \\ & 122{\cdot}6 \end{aligned}$$

$$\text{Percentage amount of K} = \frac{39{\cdot}1 \times 100}{122{\cdot}6} = 31{\cdot}89$$

$$\text{,,} \quad \text{,,} \quad \text{Cl} = \frac{35{\cdot}5 \times 100}{122{\cdot}6} = 28{\cdot}95$$

$$\text{,,} \quad \text{,,} \quad \text{O} = \frac{48 \times 100}{122{\cdot}6} = \underline{39{\cdot}16}$$

$$\underline{\underline{100{\cdot}00}}$$

(12) Find the percentage amount of water of crystallisation in $FeSO_4, 7H_2O$.

$$\begin{aligned} Fe &= 56 \\ S &= 32 \\ O_4 &= 64 \\ 7H_2O &= \underline{126} \\ & 278 \end{aligned}$$

278 parts of $FeSO_4, 7H_2O$ contain 126 parts of water.

$$\text{Percentage of water} = \frac{126 \times 100}{278} = 45{\cdot}32.$$

468. **Determination of the Formula of a Substance.**—The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance.

Suppose a compound of three elements, A, B, and C, contains p per cent. of the element A by weight, q per cent. of B, and r per cent. of C. Let $A_x B_y C_z$ represent the formula of the compound, x, y, and z being the relative numbers of atoms of A, B, and C respectively. Then if a, b, and c denote the atomic weights of the elements A, B, and C, we shall have ax parts by weight of A, by parts of B, and cz parts of C. But the given percentage composition shows that these parts by weight are in the ratio $p : q : r$; therefore—

$$ax : by : cz :: p : q : r;$$

$$\therefore x : y \quad z :: \frac{p}{a} : \frac{q}{b} : \frac{r}{c}.$$

Hence, if we divide the percentage amount of each element by the atomic weight of the element, and reduce the ratio of the numbers so obtained to its simplest form, we obtain the ratio $x : y : z$ in its simplest form.

(13) For example, suppose the percentage composition of a body as deduced from analysis is—

$$\begin{aligned} \text{Sulphur} &= 23{\cdot}7 \text{ per cent.} \\ \text{Oxygen} &= 23{\cdot}7 \quad ,, \quad ,, \\ \text{Chlorine} &= \underline{52{\cdot}6} \quad ,, \quad ,, \\ & \quad \underline{\underline{100{\cdot}0}} \end{aligned}$$

Dividing the percentage of each element by its atomic weight we have—

$$S = 32. \quad \frac{23{\cdot}7}{32} = 0{\cdot}74.$$

$$O = 16. \quad \frac{23{\cdot}7}{16} = 1{\cdot}48.$$

$$Cl = 35{\cdot}5. \quad \frac{52{\cdot}6}{35{\cdot}5} = 1{\cdot}48.$$

Dividing the numbers so obtained by their highest common factor*—which is obviously 0·74—we obtain the relative number of atoms of each element in whole numbers.

$$S. \quad \frac{0{\cdot}74}{0{\cdot}74} = 1.$$

$$O. \quad \frac{1{\cdot}48}{0{\cdot}74} = 2.$$

$$Cl. \quad \frac{1{\cdot}48}{0{\cdot}74} = 2.$$

The simplest formula for the compound is therefore—

$$S_1O_2Cl_2 \quad \text{or} \quad SO_2Cl_2.$$

This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula should be $S_2O_2Cl_4$, or $S_3O_6Cl_6$, or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *molecular formula* of the body.

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* The highest common factor can generally be seen by inspection.

In the case under consideration the vapour density of the compound is 67·5, corresponding to a molecular weight of 67·5 × 2 or 135.

Now—

$$\begin{aligned} SO_2Cl_2 &= 32 + 2 \times 16 + 2 \times 35\cdot5 \\ &= 135. \end{aligned}$$

The molecular formula for the compound is therefore the same as its empirical formula, *i.e.* SO_2Cl_2.

(14) Find the formula of a substance having the composition—

$$\begin{aligned} Mg &= 9\cdot76 \\ S &= 13\cdot01 \\ O &= 26\cdot01 \\ \text{Water of crystallisation} &= \underline{51\cdot22} \\ & \underline{\underline{100\cdot00}} \end{aligned}$$

Here we proceed as before, except that the relative number of *molecules* of water of crystallisation is found by dividing by the *molecular weight* of water—

$$\text{Mg.}\quad \frac{9\cdot76}{24} = 0\cdot406.$$

$$\text{S.}\quad \frac{13\cdot01}{32} = 0\cdot406.$$

$$\text{O.}\quad \frac{26\cdot01}{16} = 1\cdot626.$$

$$H_2O.\quad \frac{51\cdot22}{18} = 2\cdot846.$$

Dividing by the lowest number we have—

$$\text{Mg.}\quad \frac{0\cdot406}{0\cdot406} = 1.$$

$$\text{S.}\quad \frac{0\cdot406}{0\cdot406} = 1.$$

$$\text{O.}\quad \frac{1{\cdot}626}{0{\cdot}406} = 4.$$

$$\text{H}_2\text{O.}\quad \frac{2{\cdot}816}{0{\cdot}406} = 7.$$

The simplest formula for the compound is therefore—

$$MgSO_4,\ 7H_2O.$$

469. **Application to Chemical Problems.**—We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

(15) What weight of caustic soda (NaOH) will be needed to just neutralise 10 c.c. of dilute sulphuric acid (sp. gr. 1·155) containing 21 per cent. of H_2SO_4?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—

$$2NaOH + H_2SO_4 = \underset{\text{Sodium sulphate}}{Na_2SO_4} + 2H_2O.$$

From this we see that 2NaOH neutralise H_2SO_4, the respective weight relations being—

$$2\ (23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 94.$$

80 parts by weight of caustic soda serve to neutralise 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralised—

10 c.c. of the dilute sulphuric acid (sp. gr. 1·155) weigh 11·55 grams.

21 per cent. of this is H_2SO_4, *i.e.* $\frac{11{\cdot}55 \times 21}{100} = 2{\cdot}426$ grams.

Required amount of caustic soda is—

$$\frac{2{\cdot}426 \times 80}{98} \text{ grams, or } 1{\cdot}98 \text{ grams.}$$

(16) What volume of oxygen collected at standard temperature and pressure (0° and 760 mm.) is given off on heating 10 grams of mercuric oxide?

The equation representing the action of heat on mercuric oxide is—

$$2HgO = 2Hg + O_2.$$

First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

10 grams, therefore yield $\frac{2 \times 10}{27}$, or 0·74 gram.

Now 32 grams of oxygen occupy at standard temperature and pressure 22·22 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0{\cdot}74 \times 22{\cdot}22}{32} = 514 \text{ cubic centimetres.}$$

(17) What weight of sulphur must be burnt so as to yield 1 litre of sulphur dioxide at standard temperature and pressure?

$$S + O_2 = SO_2.$$

Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22·22 litres of SO_2 weigh 64 grams.

$\therefore$ 1 litre of SO_2 weighs $\frac{64}{22{\cdot}22}$ or 2·869 grams.

Also 64 grams of SO_2 contain 32 grams of S,

$\therefore$ 2·869 „ SO_2 „ 1·4345 „ S.

1·4345 grams of sulphur will therefore be required to produce 1 litre of SO_2.

Such a calculation may, however, be shortened by the consideration that as 32 grams of sulphur, according to the equation, yield 64 grams or 22·22 litres of SO_2,

$\frac{32}{22{\cdot}22}$ grams will yield 1 litre of SO_2.

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really involved, except that the correction for temperature and pressure must be made.

(18) 2½ litres of nitrous oxide have been collected at 39° C. and 741 mm. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2{\cdot}5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2{\cdot}133 \text{ litres.}$$

Now according to the equation—

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{Nitrous oxide}}{N_2O} + 2H_2O,$$

80 grams of ammonium nitrate yield 44 grams (or 22·22 litres) of nitrous oxide, and hence

$$\frac{80 \times 2{\cdot}133}{22{\cdot}22} \text{ grams, or } 7{\cdot}681 \text{ grams, of ammonium}$$

nitrate have been decomposed.

(19) One gram of water is (*a*) converted into steam at 100° C., (*b*) decomposed by means of sodium and the hydrogen collected at 13° C.; what volume will each occupy, the barometer at the time standing at 750 mm.?

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

18 grams is the weight of 22·22 litres.

$$\text{Thus 1 gram occupies } \frac{22{\cdot}22}{18} \text{ or } 1{\cdot}234 \text{ litres.}$$

At 100° C. and 750 mm. pressure this occupies—

$$\frac{1{\cdot}234 \times 373 \times 760}{273 \times 750} = 1{\cdot}71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—

$$2Na + 2H_2O = 2NaOH + H_2;$$

from which we see that 36 grams of water yield 2 grams of hydrogen, and therefore 1 gram of water yields $\frac{1}{18}$ gram of hydrogen.

The *volume* of hydrogen at standard temperature and pressure is thus $\frac{11 \cdot 11}{\cdot 18}$ or 0·62 litre. Corrected so as to represent the volume at 13° C. and 750 mm. pressure this becomes—

$$\frac{0 \cdot 62 \times 286 \times 760}{273 \times 750} = 0 \cdot 658 \text{ litre.}$$

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some examples in further illustration of their application to chemical reactions.

(20) 10 grams. of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at 15° C. and 765 mm. pressure; what volume does it occupy?

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.

$$Hg + 2H_2SO_4 = \underset{\text{Mercuric sulphate}}{HgSO_4} + 2H_2O + SO_2.$$

200 grams of mercury give 64 grams of SO_2,
or 200 „ „ „ 22·22 litres of SO_2,
∴ 10 „ „ „ 1·111 „ „

at standard temperature and pressure.

Volume at 15° C. and 765 mm. pressure is then

$$\frac{1 \cdot 111 \times 288 \times 760}{273 \times 765} = 1 \cdot 164 \text{ litre.}$$

(21) 25 c.c. of marsh gas (CH_4) are mixed with 500 c.c. of air and exploded in a eudiometer; what volume of gas should there be (*a*) before the removal of the carbon dioxide formed, (*b*) after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume were taken.

The chemical reaction which takes place is

$$\underset{2\text{ vol.}}{CH_4} + \underset{4\text{ vol.}}{2O_2} = \underset{2\text{ vol.}}{CO_2} + 2H_2O,$$

the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.c., and is represented by 2 volumes.

The diminution in volume is therefore 50 c.c., and the 525 c.c. of mixed gases originally present in the eudiometer have been reduced to 475 c.c.

Similarly the carbon dioxide occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.c., and if this be removed there will remain 450 c.c. of gas in the eudiometer. The result is that the residual gas—

(*a*) before removal of CO_2 is 475 c.c.
(*b*) after ,, ,, ,, 450 c.c.

(22) 10 c.c. of liquid carbon bisulphide (sp. gr. 2·63) are burnt in oxygen; find the volume of the resulting gases measured at standard temperature and pressure.

We must first ascertain the weight of the carbon bisulphide. Its sp. gr. being 2·63, the 10 c.c. will weigh 26·3 grams.

The chemical change during combustion is represented in the equation—

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

76 grams of CS_2 yield 44 grams or 22·22 litres CO_2.
,, ,, ,, ,, 128 ,, ,, 44·44 ,, SO_2.
,, ,, ,, ,, 66·66 litres of CO_2 and SO_2 together.

$$26{\cdot}3 \text{ grams of } CS_2 \text{ yield } \frac{66{\cdot}66 \times 26{\cdot}3}{76} = 23{\cdot}08 \text{ litres.}$$

(23) Considering air as a mixture of 79 per cent. by volume of nitrogen with 21 per cent. by volume of oxygen

(*i.e.* neglecting argon), find the density of air compared with hydrogen. Also find the density of the vapour of carbon bisulphide compared with air.

79 vol. of nitrogen are as heavy as 79 × 14, or 1,106 vol. of H.

21 vol. of oxygen are as heavy as 21 × 16, or 336 vol. of H.

100 vol. of air are as heavy as ... ... 1,442 vol. of H.

∴ Density of air is 14·42. *

Density of the vapour of bisulphide of carbon is $\frac{12 + 64}{2}$ or 38, compared with hydrogen.

Compared with air it is therefore $\frac{38}{14 \cdot 42} = 2 \cdot 635$.

QUESTIONS.—CHAPTER XXXIII.

[N.B.—In the following calculations use the atomic weights in the table on p. 103.]

1. The volume of a permanent gas at 0° C. is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?
2. Two samples of gas occupy the same volume, but one is at – 20° C., and the other at 20° C.; what is their relative volume when both are at 0° C.?
3. The volume of a gas at 13° C. is 100 c.c.; find its volume at – 130° C., at – 13° C., and at 130° C.
4. A gas under standard atmospheric pressure measures 209 c.c.; what volume will it occupy under a pressure of $\frac{1}{10}$, $\frac{1}{2}$, 2, and $5\frac{1}{2}$ atmospheres respectively?
5. What volume will half a litre of gas measured at 750 mm. pressure occupy when subjected to a pressure of 850 mm. of mercury?

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* Actual density at normal composition is taken as 14·435.

6. A rectangular vessel 10 cm. long, 5 cm. wide, and 3·5 cm. deep, is filled with gas at 100° C. and 770 mm. pressure; what volume will the gas occupy at standard temperature and pressure?

7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 mm. above that in the trough; also the height of the barometer at the time is 745 mm.; under what pressure is the gas?

8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?

9. Under how many atmospheres pressure will steam have the same density as water (1 c.c. weighs one gram), if the contraction takes place in accordance with Boyle's law, and the temperature remains at 600° C.?

10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0·62 of that of water?

11. One cubic centimetre of bromine (density 3·2) is transformed into vapour at 78° C.; determine the volume occupied by the vapour.

12. The sp. gr. of pure nitric acid being 1·522, find the weight of 100 c.c. of it, and the volume that you must take to weigh 100 grams.

13. What volume of such acid will be required to just neutralise 100 grams of caustic potash (KOH), and what weight of potassium nitrate will be formed?

14. Calculate the percentage composition of calcium carbonate; what percentage of carbon dioxide does it contain?

15. Chlorine forms with water a solid hydrate, having the composition $Cl_2, 8H_2O$; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.

16. Find the empirical formula of a compound consisting of 46·66 per cent. of iron and 53·33 per cent. of sulphur.

17. An oxide of iron contains 72·3 per cent. of iron; determine its empirical formula.

18. Determine the simplest formula for a salt having the following percentage composition:—

Sodium,	29.36
Phosphorus,	26·38
Oxygen,	44·26
	100·00

19. A solution of caustic soda having the sp. gr. 1·32 contains 28·8 per cent. of NaOH; what weight of sulphuric acid is required to be just sufficient to neutralise a litre of such a solution?

20. What volume of sulphuretted hydrogen at 13° C. and 798 mm. pressure is required to effect the complete precipitation of one gram of corrosive sublimate, $HgCl_2$?

21. What weight of pure antimony sulphide, Sb_2S_3, should yield a litre of sulphuretted hydrogen collected at 10° C. and 760 mm. pressure?

22. Determine the volume of chlorine required to convert 10 grams of phosphorus into the pentachloride.

23. A gram of common salt is dissolved in water and excess of silver nitrate solution is added; what weight of silver chloride should be precipitated?

24. Calculate (*a*) the volume, (*b*) the weight, of carbon dioxide in the air of a room 6 metres long, 4 metres wide and 3 metres high, if there is 1 volume of this gas present per 1,000 volumes of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment,	120	grm.
„ „ „ after „	121 15	„
„ globe when exhausted	852	„
„ „ and nitrogen	855·85	„

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume.

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment,	334·598	grm.
„ „ „ „ after „	314·238	„
„ drying tubes before experiment... ...	426·358	„
„ „ „ after „	449·263	„

Calculate the percentage composition of water by weight.

27. Ten grams of steam are passed over red-hot iron; what volume of hydrogen at 26° C. and 741 mm. pressure will be obtained if one-third of the steam undergoes decomposition?

28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.c. of oxygen are added and the mixed gases exploded; state the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.

29. A mixture of ten litres of oxygen with one litre of carbon dioxide is shaken up with 100 c.c. of water; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 mm. and the thermometer at zero.

30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.

31. A litre of sea-water (sp. gr. 1·03) is evaporated to dryness, and found to leave as residue 36·4 grams of salts; find the percentage of solid matter in the sea-water.

32. Given that a metre is equivalent to 39·37 inches, calculate the number of cubic inches in a litre, and the number of litres in a cubic foot.

33. Determine the percentage of carbon in cane-sugar ($C_{12}H_{22}O_{11}$) and the volume of carbon dioxide that results from the combustion of 0·2 gram of sugar.

34. A mixture of 20 c.c. of ethylene and 200 c.c. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?

35. What quantity of crystallised oxalic acid ($C_2H_2O_4 + 2H_2O$), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?

36. If 50 c.c. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrogen chloride will be formed, and what weight of sulphur liberated?

37. A gram of a substance containing carbon is heated with lead monoxide, and found to form 10 grams of metallic lead; what percentage of carbon was present?

38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cubic metres?

39. Ten grams of carbon are burnt in 1,000 litres of air (taken as consisting of 79 vol. of N and 21 of O) at 15° C. and 700 mm. pressure; find the percentage of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

APPENDIX I.

COPPER.

470. **Occurrence.**—Copper is found as the *metal* in considerable quantity in the neighbourhood of Lake Superior, also in smaller amount in some other parts of the American continent, in Cornwall, and in Siberia and the Ural mountains; as *cuprous oxide*, Cu_2O, in the mineral cuprite it is found in Cornwall, South America, and Australia; as *cuprous sulphide*, Cu_2S, in copper glance, and associated with sulphide of iron in copper pyrites, $Cu_2S.Fe_2S_3$; as *basic carbonate* in malachite, $CuCO_3.Cu(OH)_2$, and in azurite, $2\,CuCO_3.Cu(OH)_2$.

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the ferrous oxide enters into combination with the silica, either already contained in the ore or added to the charge, to form a slag of ferrous silicate. By repetition of the roastings and fusions the iron is ultimately removed.

$$
\begin{array}{lllll}
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(b) & Cu_2O & + FeS & = FeO & + Cu_2S \\
(c) & FeO & + SiO_2 & = FeSiO_3 & \text{(slag)} \\
(d) & 2\,Cu_2S & + 3\,O_2 & = 2\,Cu_2O & + 2\,SO_2
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(2) At a moderate temperature the cuprous sulphide is then partially oxidized, and the temperature is raised so that the cuprous oxide formed may react with the sulphide—

$$2\,Cu_2O + Cu_2S = 6\,Cu + SO_2.$$

The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron which still remains is also acted upon by the cuprous oxide as follows—

$$3\,Cu_2O + FeS = 6\,Cu + FeO + SO_2.$$

(3) *The refining.*—The crude copper ("blister copper") is fused in an oxidizing atmosphere on the bed of the refining furnace and impurities, such as arsenic, sulphur, iron, antimony, etc., still remaining are oxidized and skimmed off as a slag. Finally anthracite is sprinkled on the surface of the molten metal and agitation and admixture promoted by stirring the mass with "green" poles of wood. In this way the reduction of any remaining cuprous oxide is effected and particles of slag are carried to the surface.

On the Continent and in America it is now very usual to calcine the ore to the oxide, and then effect the reduction with coke in a form of blast furnace.

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copper are suspended in a tank or series of tanks containing a solution of sulphate of copper to which sulphuric acid is added. These constitute the anodes, and the kathodes on which, during the passage of the current, the pure copper deposits consist of thin sheet copper. The impurities pass into solution with the exception of the silver and gold, which collect as a slime at the bottom of the tank. By this method therefore it is possible not only to obtain copper of a very high degree of purity (over 99·8 per cent.), but also to recover the silver and gold. About 60 per cent. of the total output of copper is now refined electrically.

473. **Properties of Metallic Copper.**—The metal has a red colour by reflected light and in thin plates it transmits green light. Its specific gravity is 8·95; when heated and allowed to cool slowly it is brittle, but if cooled rapidly it is much softer and highly malleable and ductile. With the exception of silver, it is the best conductor of heat and electricity known. It possesses considerable tenacity, but this falls off rapidly when it is heated; it melts at 1080° C., and at very high temperatures it may even be distilled. Dry air is without action upon it, at ordinary temperatures, but in presence of moisture and carbon dioxide it becomes corroded and coated with a deposit of basic carbonate, commonly called *verdigris*. Hydrochloric and sulphuric acids have no action on copper in the cold if air is excluded; the metal is, however, attacked by the hot concentrated acids, slowly in the case of hydrochloric acid and rapidly in that of sulphuric acid (p. 273). Nitric acid, whether dilute or concentrated, acts readily on copper even in the cold (p. 229).

Alloys.—With zinc it forms brass, and with tin, bell metal, gun metal, speculum metal and bronze, the latter often containing also zinc or lead.

474. **The Oxides and Hydroxide.**—The lower oxide, *cuprous oxide*, Cu_2O, occurs native as cuprite, a mineral which crystallizes in octahedra. It is also found amongst the products obtained in the extraction of copper in deep

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Exp. 221.—Add to a solution of cupric sulphate some Rochelle salt (sodium potassium tartrate), then potash, and finally grape sugar. Warm gently, and note the formation of a red precipitate. Decant off the liquid after settling, and add ammonia to the residue. Note what happens.

The solutions of cuprous salts are in general colourless, but they are very unstable and rapidly absorb oxygen from the air and turn blue, owing to their transformation into cupric salts.

Cupric Oxide, CuO, is a black oxide obtained by oxidation of the metal or by heating the hydroxide, carbonate or nitrate. At high temperatures it loses oxygen and is converted into cuprous oxide or a lower oxide, Cu_3O. Hydrogen, carbon monoxide, or other reducing agents undergo oxidation in contact with heated cupric oxide, and it is therefore used in the analysis of organic substances, the carbon and hydrogen of which are converted into carbon dioxide and water respectively. Cupric oxide dissolves in molten glass, imparting a green colour to it, whilst cuprous oxide gives it a ruby-red tint.

The *hydroxide*, $Cu(OH)_2$, is obtained as a greenish bulky precipitate, when caustic potash is added to cupric salts in the cold. On boiling, the precipitate turns black, since at moderate temperatures the hydroxide gives up water and is converted into the black cupric oxide. It dissolves in ammonia to a deep blue solution which has the property of dissolving cellulose (filter paper).

475. **Cuprous Sulphide, Cu_2S,** is the "white metal" obtained in the metallurgy of copper; it may be prepared by exposing finely-divided copper or copper foil to sulphur vapour. It is also obtained when cupric sulphide, CuS, is heated with sulphur in a stream of hydrogen.

The apparatus usually employed for the reduction is shown in Fig. 95. A stream of hydrogen dried by being passed through the vessel A containing strong sulphuric acid is led into a crucible containing the cuprous sulphide and sulphur by a porcelain tube which passes through a perforation in the crucible lid (Rose's Crucible). Complete reduction is known to have taken place when the weight of the crucible and contents becomes constant. Cuprous sulphide crystallizes both in the regular and rhombic system and is isodimorphous with the corresponding sulphide of silver, with which it often occurs associated in the mineral kingdom.

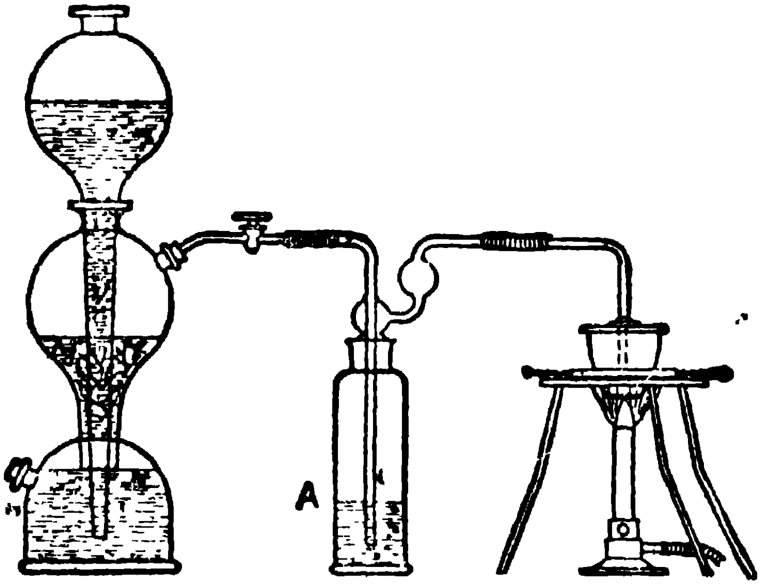

FIG. 95.

Cupric Sulphide, CuS, is the dark-brown precipitate obtained when copper salts are precipitated by sulphuretted hydrogen. When exposed to air in the moist condition it gradually oxidizes to cupric sulphate, and if heated in the dry condition readily passes into cuprous sulphide. It may be completely converted into Cu_2S by the method described in the preceding paragraph.

476. Haloid Salts.—Copper forms also two series of haloid salts, the cuprous, Cu_2F_2, Cu_2Cl_2, etc., and the cupric, CuF_2, $CuCl_2$, etc. The latter salts, though in general tolerably stable in solution and obtainable therefrom on concentration in crystals, are readily decomposed by heat and converted into the cuprous form, in which they are insoluble in water. The cupric iodide, however, breaks up even in the moist condition, and the precipitate obtained on adding potassium iodide to solutions of cupric salts consists of white cuprous iodide and iodine. Cuprous salts give under the same circumstances a pure white precipitate of cuprous iodide.

477. **Cuprous Chloride, Cu_2Cl_2,** is formed by burning copper in chlorine or by the action of reducing agents such as stannous chloride, $SnCl_2$, zinc dust or metallic copper on cupric chloride. If therefore cupric oxide be dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green owing to the formation of a basic chloride. It may also be conveniently prepared by the method described in the following experiment.

Preparation of Cuprous Chloride.—

Exp. 222.—To a strong solution of copper sulphate add common salt and concentrated hydrochloric acid. Boil this solution for some time with copper turnings. Pour off the liquid from the unused copper and add water till a white precipitate is thrown down. This is cuprous chloride, which is insoluble in water but soluble in a strong solution of HCl. Collect the precipitate by filtration, and wash with water. Press it between filter paper and dry it in a steam oven.

The solution of cuprous chloride in ammonia absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2, cuprous acetylide, Cu_2C_2, is formed, from which pure acetylene may be liberated by treatment with acid. Cuprous chloride volatilizes at high temperatures and its vapour density corresponds to the formula Cu_2Cl_2.

Cupric Chloride, $CuCl_2$, is formed when copper or cuprous chloride is heated in excess of chlorine. It is a brown deliquescent powder dissolving readily in water with formation of a green liquid, which changes to blue on further dilution. From this liquid greenish-blue crystals (rhombic prisms) having the composition $CuCl_2, 2H_2O$ separate out on evaporation. Cupric chloride may also be obtained by dissolving cupric oxide in hydrochloric acid. Several oxychlorides are known, one of which is the product obtained by the action of a small quantity of bleaching powder on a solution of cupric sulphate; it is used as the pigment Brunswick green.

Cuprous Iodide, Cu_2I_2.—When potassium iodide solution is added to a *cupric* salt a precipitate is formed which is not, as one would expect, cupric iodide, but cuprous iodide.

Exp. 223.—To a solution of copper sulphate add KI solution till no further precipitation occurs. Note that the solution is brown. Test this solution with starch. A blue coloration will be obtained denoting the presence of free iodine. Filter off the precipitate, wash it with water, and then with a little alcohol, which dissolves the iodine. A white crystalline powder remains, which is cuprous iodide.

The reaction is expressed by the following equation—

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

We thus see that half the iodine is liberated in the free state. It is obvious that this reaction might be employed to estimate copper indirectly, *i.e.* by first estimating the iodine, and it does in fact constitute one of the methods of estimating copper. The formation of the iodine might be prevented by the addition of a ferrous salt or of sulphurous acid. The formation of Cu_2I_2 on addition of KI to a solution of a copper salt has been employed in the separation of the iodide from a mixture of iodide with chloride or bromide or both.

478. **Cupric Sulphate, $CuSO_4$.**—This salt may be obtained in the form of blue triclinic crystals of the composition $CuSO_4.5H_2O$ by dissolving cupric oxide in sulphuric acid and allowing the solution to crystallize. Copper sulphate is prepared on a commercial scale from copper pyrites, $CuFeS_2$. By careful roasting the copper is converted

into the sulphate and the iron into oxide. On lixiviation the copper sulphate goes into solution, from which it may be obtained by crystallization. Prepared in this way the crystals always contain a small quantity of ferrous sulphate; but the presence of the iron salt is not objectionable for some purposes for which blue vitriol is usually employed. To obtain the pure copper sulphate the metal is precipitated by addition of iron and this is dissolved in sulphuric acid. By gently heating, the hydrated salt loses water and is converted into anhydrous cupric sulphate, a white powder which readily takes up moisture from the air and may be used as a desiccating agent.

479. **Detection and Estimation.**—Copper compounds give a bluish-green or emerald-green colour to the Bunsen flame. Copper compounds are easily reduced on charcoal to the metallic condition. They are precipitated by sulphuretted hydrogen as cupric sulphide insoluble in dilute mineral acids.

The methods of estimating copper are numerous. When convenient it may be estimated as oxide by first precipitating as hydrate and boiling. The method described under cuprous sulphide is perhaps the most reliable for general purposes. A method, which in some cases is convenient, consists in the deposition of metallic copper either by immersion of iron in the solution or electrolytically.

QUESTIONS.—APPENDIX I.

1. Give the names and formulæ of some of the more important compounds of copper which occur native. Describe briefly the processes by which the metal is extracted.

2. How would you prepare both cuprous and cupric oxides from metallic copper, and how could you obtain the metal from them again?

3. How is cupric sulphide obtained? What happens to it if it is left exposed to the air in a moist state? How may it be converted into the cuprous compound?

4. Give methods for the preparation of cuprous chloride. Compare the behaviour of the two chlorides of copper towards water and ammonia respectively.

5. By what process is copper sulphate obtained on the large scale? What impurity is the commercial product likely to contain? How would you propose to remove it? What happens (*a*) when copper sulphate crystals are heated, (*b*) when the solution of the crystals is added to strong hydrochloric acid, (*c*) when ammonium hydroxide is added to this solution?

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the ferrous oxide enters into combination with the silica, either already contained in the ore or added to the charge, to form a slag of ferrous silicate. By repetition of the roastings and fusions the iron is ultimately removed.

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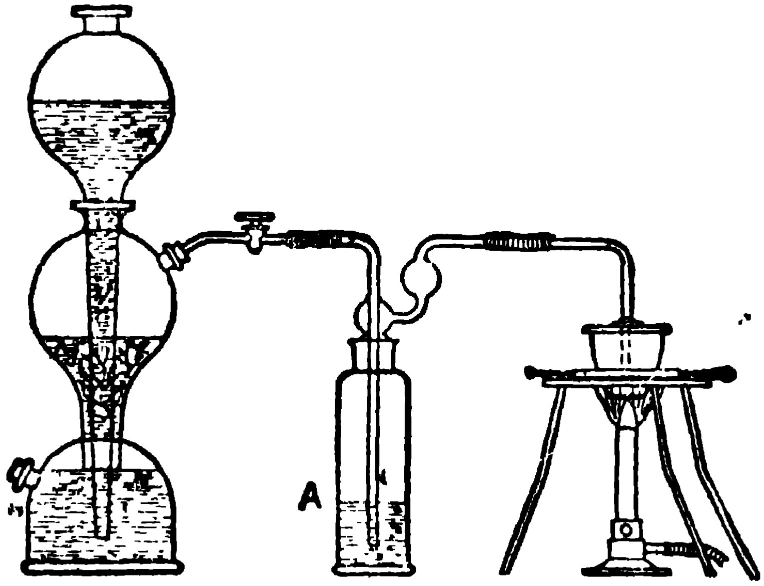

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The solution of cuprous chloride in ammonia absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2, cuprous acetylide, Cu_2C_2, is formed, from which pure acetylene may be liberated by treatment with acid. Cuprous chloride volatilizes at high temperatures and its vapour density corresponds to the formula Cu_2Cl_2.

Cupric Chloride, $CuCl_2$, is formed when copper or cuprous chloride is heated in excess of chlorine. It is a brown deliquescent powder dissolving readily in water with formation of a green liquid, which changes to blue on further dilution. From this liquid greenish-blue crystals (rhombic prisms) having the composition $CuCl_2, 2H_2O$ separate out on evaporation. Cupric chloride may also be obtained by dissolving cupric oxide in hydrochloric acid. Several oxychlorides are known, one of which is the product obtained by the action of a small quantity of bleaching powder on a solution of cupric sulphate; it is used as the pigment Brunswick green.

Cuprous Iodide, Cu_2I_2.—When potassium iodide solution is added to a *cupric* salt a precipitate is formed which is not, as one would expect, cupric iodide, but cuprous iodide.

Exp. 223.—To a solution of copper sulphate add KI solution till no further precipitation occurs. Note that the solution is brown. Test this solution with starch. A blue coloration will be obtained denoting the presence of free iodine. Filter off the precipitate, wash it with water, and then with a little alcohol, which dissolves the iodine. A white crystalline powder remains, which is cuprous iodide.

The reaction is expressed by the following equation—

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

We thus see that half the iodine is liberated in the free state. It is obvious that this reaction might be employed to estimate copper indirectly, *i.e.* by first estimating the iodine, and it does in fact constitute one of the methods of estimating copper. The formation of the iodine might be prevented by the addition of a ferrous salt or of sulphurous acid. The formation of Cu_2I_2 on addition of KI to a solution of a copper salt has been employed in the separation of the iodide from a mixture of iodide with chloride or bromide or both.

478. **Cupric Sulphate, $CuSO_4$.**—This salt may be obtained in the form of blue triclinic crystals of the composition $CuSO_4.5H_2O$ by dissolving cupric oxide in sulphuric acid and allowing the solution to crystallize. Copper sulphate is prepared on a commercial scale from copper pyrites, $CuFeS_2$. By careful roasting the copper is converted

into the sulphate and the iron into oxide. On lixiviation the copper sulphate goes into solution, from which it may be obtained by crystallization. Prepared in this way the crystals always contain a small quantity of ferrous sulphate; but the presence of the iron salt is not objectionable for some purposes for which blue vitriol is usually employed. To obtain the pure copper sulphate the metal is precipitated by addition of iron and this is dissolved in sulphuric acid. By gently heating, the hydrated salt loses water and is converted into anhydrous cupric sulphate, a white powder which readily takes up moisture from the air and may be used as a desiccating agent.

479. **Detection and Estimation.**—Copper compounds give a bluish-green or emerald-green colour to the Bunsen flame. Copper compounds are easily reduced on charcoal to the metallic condition. They are precipitated by sulphuretted hydrogen as cupric sulphide insoluble in dilute mineral acids.

The methods of estimating copper are numerous. When convenient it may be estimated as oxide by first precipitating as hydrate and boiling. The method described under cuprous sulphide is perhaps the most reliable for general purposes. A method, which in some cases is convenient, consists in the deposition of metallic copper either by immersion of iron in the solution or electrolytically.

QUESTIONS.—APPENDIX I.

1. Give the names and formulæ of some of the more important compounds of copper which occur native. Describe briefly the processes by which the metal is extracted.

2. How would you prepare both cuprous and cupric oxides from metallic copper, and how could you obtain the metal from them again?

3. How is cupric sulphide obtained? What happens to it if it is left exposed to the air in a moist state? How may it be converted into the cuprous compound?

4. Give methods for the preparation of cuprous chloride. Compare the behaviour of the two chlorides of copper towards water and ammonia respectively.

5. By what process is copper sulphate obtained on the large scale? What impurity is the commercial product likely to contain? How would you propose to remove it? What happens (*a*) when copper sulphate crystals are heated, (*b*) when the solution of the crystals is added to strong hydrochloric acid, (*c*) when ammonium hydroxide is added to this solution?

APPENDIX II.

THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

THE metric system has been found the most convenient for operations in which weighing and measuring are concerned, and it is universally used in scientific work.

The *unit of length* in this system is the *metre*, which is equivalent to 39·37 inches.

The *unit of volume* is that of a cube whose side is $\frac{1}{100}$ of a metre, equivalent to very nearly one-sixteenth of a cubic inch, and the *unit of weight* is the weight of this volume of water, the temperature being that at which water has its maximum density, viz. 4° C. This weight is termed the *gramme*, and is equivalent to 15·432 grains.

The prefix *kilo* indicates the multiple 1,000, thus—

1 kilogramme = 1,000 grammes = 15,432 grains =
about 2·2 lbs.

The prefixes *deci*, *centi*, and *milli* respectively indicate the fractional parts $\frac{1}{10}$, $\frac{1}{100}$ and $\frac{1}{1000}$.

1 decimetre = $\frac{1}{10}$ metre = 3·937 inches.
1 centimetre = $\frac{1}{100}$ " = 0·3937 "
1 millimetre = $\frac{1}{1000}$ " = 0·03937 "

One inch is thus slightly more than 25 millimetres.

1 decigramme = $\frac{1}{10}$ gramme = 1·5432 grains.
1 centigramme = $\frac{1}{100}$ " = 0·15432 "
1 milligramme = $\frac{1}{1000}$ " = 0·015432 "

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogramme of water at 4° C.; it is therefore equivalent to a cubic decimetre, or, in English measure, 61·027 cubic inches.

APPENDIX III.

TABLES FOR REDUCTION OF MOIST GAS TO STANDARD CONDITIONS.

THE volume of a moist gas having been measured at a given temperature and pressure it is necessary to first find what volume the *dry* gas would occupy at 0° C. and 760 mm. pressure. Allowance must be made (see Chaps. VIII, XIII)—

(*a*) for the temperature of the gas (*i e.* of the room);
(*b*) for the pressure to which it is subject (that of the atmosphere at the time of the experiment);
(*c*) the tension of water-vapour.

This involves a somewhat complex calculation, and a table has therefore been drawn up to enable the student to make the correction by using the factor given in the table.

Thus suppose the temperature of the laboratory to be 10° C. and the atmospheric pressure 740 m.m.; the tension of aqueous vapour with which the gas is saturated is for 10° C., 9·1 mm. Now if v is the volume of the moist gas as observed, then V the volume of the dry gas at 0° C. and 760 mm. pressure is given by the expression—

$$V = \frac{v \times 273 \times (740 - 9{\cdot}1)}{283 \times 760} = 0{\cdot}928\, v.$$

To deduce the volume of the dry gas at standard temperature and pressure from the observed volume it is therefore only necessary to *multiply this latter by the factor* 0·928 as taken from the table, and so for any other temperature or pressure.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0·915	0·907	0·899	0·891	0·882	0·874
740 mm.	0·928	0·920	0·911	0·903	0·895	0·886
750 mm.	0·940	0·932	0·924	0·915	0·907	0·898
760 mm.	0·953	0·945	0·936	0·928	0·919	0·910
770 mm.	0·966	0·957	0·949	0·940	0·932	0·923

For intermediate temperatures or pressures, the value may be expressed with sufficient accuracy by taking the proportional mean; *e. g.* for 10° C. and 745 mm. we shall find 0·934, and for 11° C. and 750 mm. we shall find 0·936.

If we desire to know the *weight* of the hydrogen liberated, the following table may be used. Taking the weight of a litre of dry hydrogen under standard conditions as 0·09 gramme the table gives the weight of hydrogen in a litre of the moist gas collected at the temperature and pressure given.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0·0824	0·0816	0·0809	0·0802	0·0794	0·0787
740 mm.	0·0835	0·0828	0·0820	0·0813	0·0806	0·0798
750 mm.	0·0846	0·0839	0·0832	0·0824	0·0816	0·0808
760 mm.	0·0858	0·0851	0·0843	0·0835	0·0827	0·0820
770 mm.	0·0869	0·0861	0·0854	0·0846	0·0839	0·0831

An example will make the method of using the table quite clear:—

Thermometer	16° C.
Barometer	750 mm.

Observed volume of gas, 120 c.c.
The factor under 16° C. and 750 mm. is 0·0824.

$$\text{Weight of hydrogen} = \frac{0{\cdot}0824 \times 120}{1{,}000} = 0{\cdot}00988 \text{ gramme.}$$

ANSWERS TO NUMERICAL QUESTIONS.

Chap. xiii.	3.	2 vols. of hydrogen.
„	6.	11·2 grammes of hydrogen. 88·8 grammes of oxygen.
„	9.	1·61° C.
„	10.	3·195° C.
„	12.	41·3 grammes.
„	13.	1000 cal., 33 cal., 63600 cal.
„	16.	19·95, 127·5.
„	17.	Standard pressure (*a*) 449·75 c.c. (*b*) 225·25 c.c. 76 mm. pressure (*a*) 44·975 c.c. (*b*) 22·525 c.c. 3 at. pressure (*a*) 1349·25 c.c. (*b*) 675·75 c.c.
„	18.	44·975 c.c. of CO_2 and 19·475 c.c. of O_2.
Chap. xvi.	6.	19·6.
„	7.	Nitrogen 78·49 per cent. Argon 0·68 „ Oxygen 20·83 „ 100·00
„	8.	22·97.
Chap. xix.	2.	5600 c.c.
Chap. xx.	21.	Disodium hydrogen phosphate. Na_2HPO_4. 88·75 grammes.
Chap. xxi.	2.	4399 tons.
„	22.	0·57 per cent.
„	23.	1146·7 c.c.
„	24.	30 c.c. 20 c.c.
„	25.	60 c.c. of oxygen.
„	26.	85 c.c. 55 c.c. of oxygen; 20 c.c. of carbon dioxide; 10 c.c. of water vapour.
Chap. xxii.	13.	8550 c.c., 2020 c.c.
Chap. xxiv.	2.	118·5.
„	5.	3.
	7.	108.
	8.	197·5.

ANSWERS TO CHEMICAL CALCULATIONS IN CHAPTER XXXIII.

1. 91°.
2. 293 : 253.
3. 50 c.c., 90·9 c.c., 140·9 c.c.
4. 2090 c.c., 418 c.c., 104·5 c.c., 38 c.c.
5. 441 c.c.
6. 129·7 c.c.
7. 488 mm.
8. 273° C.
9. 3,947 atmospheres.
0. 6,888 atmospheres.
1. 571·4 c.c.
2. 152·2 grams; 65·7 c.c.
13. 73·9 c.c.; 180·4 grams.
14. Ca = 40 per cent.
    C = 12 „
    O = 48 „
    44 per cent.
15. H = 7·44 per cent.
    Cl = 33·02 „
    O = 59·54 „
16. FeS_2.
17. Fe_3O_4.
18. $Na_6P_4O_{13}$.
19. 465·7 grams.
20. 81·8 c.c.
21. 4·86 grams.
22. 17·91 litres.
23. 2·45 grams.
24. 72 litres; 142·6 grams.
25. Oxygen, 23; Oxygen, 20·7. Nitrogen, 77; Nitrogen, 79·3.
26. Hydrogen, 11·1.
    Oxygen, 88·9.
27. 4·622 litres.
28. (*a*) N = 7·5 c.c.
    H = 22·5 c.c.
    O = 40 0 c.c.
    (*b*) N = 7·5 c.c.
    O = 28·75 c.c.
29. Oxygen = 3·73 c.c.
    Carbon dioxide = 16·36 c.c.
30. Oxygen = 0·37 c.c.
    Carbon dioxide = 163·6 c.c.
31· 3·534 per cent.
32. 61·023; 28·317.
33. 42·1 per cent.
    0·157 litre.
34. 180 c.c.; 140 c.c.
35. 14·18 grams.
36. 100 c.c.; 0·072 gram.
37. 29 per cent.
38. 252·0 kilograms.
39. Nitrogen, 79·00 per cent.
    Oxygen, 18·88 „
    Carbon dioxide, 2·12 „

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